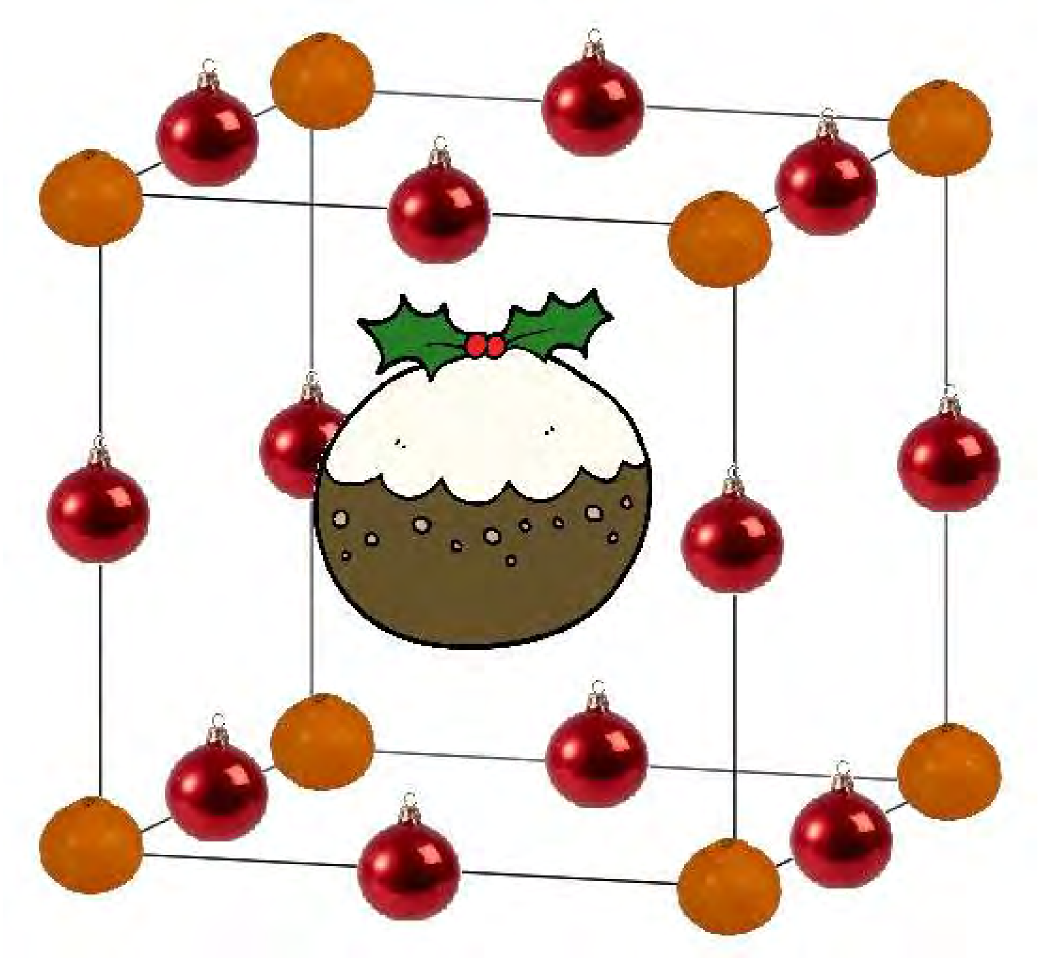
41st RSC Solid State Chemistry Group

Christmas Meeting



19-20th December 2022

University of Cambridge

UNIVERSITY OF CAMBRIDGE
Cavendish Laboratory

RSC INTEREST GROUP
SOLID STATE CHEMISTRY

We gratefully acknowledge support from the following sponsors:

RSC INTEREST GROUP
SOLID STATE CHEMISTRY

UNIVERSITY OF CAMBRIDGE
Cavendish Laboratory

HENRY ROYCE INSTITUTE

UNIVERSITY OF OXFORD

CAM-IES
Centre of Advanced Materials for Integrated Energy Systems

CrystEngComm

Dalton Transactions

Materials Advances

Materials Horizons

MATERIALS CHEMISTRY FRONTIERS

INORGANIC CHEMISTRY FRONTIERS

Welcome

On behalf of the organising committee we warmly welcome you to the 41st RSC Solid State Chemistry Group Christmas meeting.

This is the first in-person Solid State Chemistry Group Christmas meeting since 2019 and we have an attendance of over 190, with 110 posters.

We hope you enjoy the meeting and wish you all a Merry Christmas and a Happy New Year.

Organising Committee

Siân Dutton
Joshua Bocarsly
Nicola Kelly
Lauren McHugh
Liam Nagle-Cocco
Farheen Sayed
Camilla Tacconis
Chumei Ye

General Information

Meeting location

The meeting will be held in the Pippard Lecture Theatre in the Department of Physics, JJ Thomson Avenue, CB3 0HE, on the West Cambridge Campus. A registration desk will be open from 12.00 noon on Monday 19th December, located at the entrance marked by the green pin on the map below.

The first talk session will begin at 1.00 pm on Monday 19th December and the meeting finishes at lunchtime on Tuesday 20th December.

Lunch and coffee breaks will be in the foyer of the Pippard Lecture Theatre.

Toilets can be found in the corridor adjacent to the Pippard Lecture Theatre.

The Poster session will be held in the Maxwell Centre and will be signposted from the Pippard Lecture Theatre.

The conference dinner will take place on the Monday evening at Jesus College, Jesus Lane, CB5 8BL, indicated by the red pin on the map.

Internet

Internet access is available via Eduroam throughout the event. For those without Eduroam, Wi-Fi login details are available from the registration desk

Parking

Please contact sscg2022@phy.cam.ac.uk by 12.00 **noon** on **Friday 16th December** to request parking on the West Cambridge site during the event.

Conference Programme

Monday 19th December, 2022		
Noon	Registration and lunch	Pippard Lecture Theatre foyer
Session One: 1.00-2.45 pm Chair: Alex Rettie		**Pippard Lecture Theatre**
1.00 pm	Siân Dutton	Introductions and Welcome
1.15 pm	Jamie Neilson Colorado State University	Navigating Chemical Potential Landscapes for Synthetic Routes to Ternary Nitrides
2.00 pm	Bonan Zhu University College London	Locating novel polyanionic cathode materials for Li-ion batteries in underexplored chemical spaces
2.15 pm	Sandy AL Bacha University of Durham	Photocatalytic and Photocurrent Responses to Visible Light of the Lone-Pair-Based Oxysulfide $Sr_6Cd_2Sb_6S_{10}O_7$
2.30 pm	Taylor Sparks University of Utah	Revenge of the .cif: incorporating structural distance metrics into the DiSCoVeR algorithm
2.45 pm	Coffee break	Pippard Lecture Theatre foyer
Session Two: 3.30-5.00 pm Chair: Jan-Willem Bos		**Pippard Lecture Theatre**
3.30 pm	Lucy Clark University of Birmingham	Synthesis-Dependent Structure-Property Relationships of Quantum Materials
4.15 pm	Emily G. Meekel Oxford University	Truchet-tile structure of a aperiodic metal–organic framework
4.30 pm	Alexandra Morscher University of Liverpool	Control of ionic conductivity by lithium distribution in the cubic oxide argyrodites $Li_{6+x}P_{1-x}Si_xO_5Cl$
4.45 pm	Celia Castillo-Blas University of Cambridge	Formation of new crystalline qtz-[Zn(mIm)$_2$] polymorph from amorphous ZIF-8
5.00 pm	SSCG AGM	
5.00 pm	Poster Session and drinks	Maxwell Centre
7.30 pm	Conference dinner	Jesus College
Tuesday 20th December, 2022		
Session Three: 9.00-10.30 am Chair: Julia Payne		**Pippard Lecture Theatre**
9.00 am	John Kilner, Imperial College London	Grain Boundary Chemistry in Mixed Conducting Oxides
9.45 am	Otto Mustonen University of Birmingham	Evidence for a disorder-induced spin liquid in the tuneable spin ladder-chain system $Ba_2CuTe_{1-x}W_xO_6$
10.00 am	Frazer N. Forrester University of Newcastle	Disentangling Cation and Anion Dynamics in Li_3PS_4 Solid Electrolytes
10.15 am	Ady Suwardi A*STAR, Singapore	Electronic and Thermal Transport Descriptors in Thermoelectrics
10.30 am	Coffee break	Pippard Lecture Theatre foyer
Session Four: 11.00 am – 1.00 pm Chair: Donna Arnold		**Pippard Lecture Theatre**
11.15 am	Lucy Whalley Northumbria University	Steric Engineering of point defects in lead halide perovskites
noon	Thomas Hitchings University of Kent	$[C(NH_2)_3]Er(HCO_2)_2(C_2O_4)$ – The first hybrid perovskite with negative linear compressibility
12.15 pm	Keiran Orr University of Cambridge	Imaging Buried Dislocations in Halide Perovskites with 3D Strain Mapping
12.30 pm	Elizabeth Driscoll University of Birmingham	21st Century ‘White’ Gold: Extraction and Recycling
12.45 pm	Siân Dutton	Closing
1.00 pm	Lunch	Pippard Lecture Theatre foyer

Poster Presenters

1	Savyasanchi Aggarwal	PyTASER: First-principles transient absorption spectra (TAS) for bulk crystals	Imperial College London
2	Areesha Ali	Tuning between ground states in layered perovskite-related materials	University of Durham
3	Sebastian J. Altus	Increase In Critical Current Density Achieved in Li-Stuffed Garnet by Integrated Perovskite Secondary Phase	University of Sheffield
4	James Annis	Nanocrystalline Cerium Germanates For Use As Oxygen Storage Materials	University of Warwick
5	Alexander Bell	Ion Transport and Interfacial Dynamics in Thioborate Solid Electrolytes	University of Newcastle
6	Prajna Bhatt	Crystal growth of $A_3Bi_2X_9$ (A = $CH_3NH_3^+$, NH2HCNH2$^+$, Cs^+, Rb^+ and X = Cl^- , Br^- , I^-) in Silica Gel	University College London
7	Shipeng Bi	A potential thermoelectric material: zinc-based oxysulfide $SrZn_2S_2O$	University College London
8	Colm W. Boyle	Probing Li-ion Conductivity in a Material with a $Sc_2(WO_4)_3$ Framework	University of St Andrews
9	Joachim Breternitz	Tuning ternary (oxide) nitrides through disorder and composition	Helmholtz-Zentrum Berlin für Materialien und Energie
10	Katarina Brlec	A promising novel n-type thermoelectric $Y_2Ti_2O_5S_2$	University College London
11	Alexander Browne	Solid-state chemistry for quantum materials with strong spin-orbit coupling	University of St Andrews
12	Johnathan Bulled	Thermodynamic signatures of broken chains in dilute quasi-one-dimensional magnets: theory and experiment.	University of Oxford
13	Hong Cai	Fluorine-Rich Oxyfluoride Spinel $Li_{1.25}Ni_{0.625}Mn_{1.125}O_3F$ Utilizing Redox-Active Ni and Mn for High Capacity and Improved Cyclability	University of Liverpool
14	Javier Castells-Gil	Cation-disordered $LiNiO_2$ as a cathode for Li-ion batteries	University of Birmingham
15	Jiayi Cen	Exploring compounds in the Li-Ni-O space through ab initio random structure searching	University College London
16	Xin Chen	Preliminary Investigations into Anode Materials for All Solid-State Potassium-ion Batteries	University of St Andrews

17	Chris Collins	Cation Disorder and Large Tetragonal Supercell Ordering in the Li-rich Argyrodite $Li_7Zn_{0.5}SiS_6$	University of Liverpool
18	Lucia Corti	Oxide Ion Diffusion Mechanism in Melilite from ^{17}O Variable Temperature MAS and ^{71}Ga MAS NMR	University of Liverpool
19	Ana Carolina Coutinho Dutra	Defect Chemistry and Ion Transport in Low-Dimensional-Networked Li-Rich Anti-Perovskites as Solid Electrolytes for Solid-State Batteries	University of Newcastle
20	Dan Criveanu	Computational Discovery of Charge-ordered Ferroelectrics	University of Nottingham
21	Mark Crossman	Developing a Solvothermal Reaction Cell for in situ Neuron Scattering of Crystallisation	University of Warwick
22	Yun Dang	Discovery of a new lithium ion conductor in the Li-Mg-Al-P-O phase field	University of Liverpool
23	Luke Daniels	High-performance protonic ceramic fuel cell cathode using protophilic mixed ion and electron conducting material	University of Liverpool
24	Eliza Dempsey	Thermal expansion and phase transitions in niobium oxyfluorides	University of Edinburgh
25	Avishek Dey	Ionic liquids and operando photoemission spectroscopy	University College London
26	Patrick W. Doheny	Magnetocaloric Studies of a Family of Ln Adipate Metal-Organic Framework Materials	University of Kent
27	Tristan Dolling	Tuning Intra- and Inter-plane Exchange Interactions in Two-Dimensional $S = \frac{1}{2}$ Kagome Metal-Organic Frameworks	University of Birmingham
28	Bo Dong	Synthesis, Structure and Electrochemical Properties of a New Cation Ordered Layered Li-Ni-Mg-Mo Oxide	University of Birmingham
29	Wenzhen Dou	Vacancy-Regulated Charge Carrier Dynamics and Suppressed Nonradiative Recombination in Two-dimensional ReX_2 (X=S, Se)	University College London
30	Elizabeth Driscoll	Building Upon the Blocks of Battery Technology: Further Resource Development from the Birmingham Battery Bunch	University of Birmingham
31	Matthew Dyer	A Validated Dataset of Experimentally Measured Li Ion Conductivities	University of Liverpool

32	Tim Evans	Using magnetic ionic liquids as a lubricant to protect solid interfaces	University College London
33	Ehsan Ezzatpour Ghadim	An Immediate Room Temperature Synthesis Method to Form a Wide Range of Metal-Organic Frameworks for Photocatalytic Degradation	University of Warwick
34	Elisabeth Fetter	Carbon Capture and Usage: A Study of Na-doped Hydroxyapatite	University of Aberdeen
35	Nicolás Flores-González	Understanding the effect of lattice polarisability on the electrochemical properties of mechanochemically-synthesised lithium tetrahaloaluminates $LiAlX_4$ (X = Cl, Br, I)	Queen Mary University of London
36	Matthew Friskey	Investigations into Columbites as Electrode Materials for Energy Storage Devices	University of St Andrews
37	Lavan Ganeshkumar	Investigating the Effects of Doping Layered $LiNiO_2$ Cathodes	University College London
38	Alexey Y. Ganin	Mo_3Sb_7 and role of Te-doping on its electrocatalytic properties for water splitting reaction	University of Glasgow
39	Quinn Gibson	Single crystal growth and properties of the polar metallic ferromagnet $Mn_{1.05}Bi$ with Kagome layers, huge magnetic anisotropy and slow spin dynamics	University of Liverpool
40	Souvik Giri	Anion Redox as a Means to Derive Layered Manganese Oxychalcogenides with Exotic Intergrowth Structure	University of Oxford
41	Naresh Gollapally	Synthesis of faceted pristine and Mg-doped single-crystal LNO cathode materials and its electrochemical study	University of Sheffield
42	Jennifer Graham	Co-Existing Long- and Short-Range Magnetic Order in the Frustrated Diamond Antiferromagnet, $LiYbO_2$	University of Birmingham
43	Ricardo Grau-Crespo	Modelling the NMR spectra of solid solutions: DFT simulations and machine learning	University of Reading
44	Peter Gross	Alkali-rich Oxide Perovskites - A Solid-State Chemist's Playground for Exploring Structure-Property Relationships for Battery Applications	University of Sheffield
45	Bastien F. Grosso	Chemically inspired high throughput study for new stable ferroelectric nitride perovskites	University College London

46	Cara Hawkins	XPS Investigation of New Oxyfluoride Spinel Li Cathode with Redox-Active Ni and Mn	University of Liverpool
47	Abby R. Haworth	Understanding the Local Structure of Protective Alumina Coatings for Cathodes and the Coating-Cathode Interface	Imperial College London
48	Glen R. Hebberd	Exploring Stability & Synthesis of Quaternary Oxysulfides for Visible-Light Photocatalysis	University of Durham
49	Luisa Herring Rodriguez	$Sr_2Sb_2O_7$ as a novel thermoelectric material	University College London
50	Craig Hiley	Nickel (Hydroxy)Fluorides from Solution Chemistry	University of Warwick
51	Yuri Hirano	Tunability of Zero-Dimensional Organic-Inorganic Metal Halides Utilizing the m-Xylylenediammonium Cation: $MXDBiI_{5-x}Br_x$ and $MXDBiBr_{5-y}Cl_y$	University of St Andrews
52	Ju Huang	Dynamic disorder in layered covalent-organic frameworks	Imperial College London
53	Xuankai Huang	High conductivity in Na^+-ion conducting solid electrolytes for Na-ion batteries through a co-doping strategy	Imperial College London
54	Sean Injac	Stabilising Rh^{4+} Oxides through High Pressure, High Temperature Synthesis	University of Edinburgh
55	Teresa Insinna	Graphite anodes for Li-ion batteries – an EPR investigation	University of Cambridge
56	Sam Ivko	Uncovering the S = ½ Kagome Ferromagnet within a Family of Metal-Organic Frameworks	University of Birmingham
57	Adam J. Jackson	Going off-grid: alternative ways of sampling reciprocal space	STFC
58	Chandrakant Jadhav	Cobalt substitution in beta-tricalcium phosphate for biomaterial applications	University of Aberdeen
59	Xiaoyu Jia	Investigating $NaGeSbO_5$ as a transparent thermoelectric	University College London
60	Pengcheng Jing	Pillared Vanadium Molybdenum Disulfide Nanosheets; a High-performance Cathode for Magnesium-ion Batteries	University of Glasgow
61	Seán R. Kavanagh	Frenkel Excitons in Vacancy-ordered Titanium Halide Perovskites (Cs_2TiX_6)	University of Birmingham

62	Nicola Kelly	Synthesis of new layered oxychalcogenides in the AM_2Q_2O system	University of Oxford
63	Ayano Kono	Identification of Glass Transition in Glassy Titanium-based MOFs	University of Cambridge, UK and ENEOS Corporation
64	Gabriel Krenzer	Anharmonic lattice dynamics of superionic lithium nitride	Imperial College London
65	Navaratnarajah Kuganathan	Simulating volatile fission products in U(Pu)N and corresponding oxides	University of Warwick
66	Evie Ladbrook	In situ grain mapping of hybrid improper ferroelectrics under applied electric fields	University of Warwick
67	Ke Le	Computational modelling of post transition metal oxide Sb_2O_5	University College London
68	Roxy Lee	Thermal broadening in core level and valence band XPS	University College London
69	Zhenzhu Li	From cubic to hexagonal: electronic trends across metal halide perovskite polytypes	Imperial College London
70	Xia Liang	Dynamic Analysis of Hybrid Lead Halide Perovskites	Imperial College London
71	Hang Liu	Enhanced photoluminescence and reduced dimensionality via vacancy ordering in a 10H halide perovskite	University of St Andrews
72	Yuhan Liu	Phase transitions and optical properties of the trigonal perovskite $(CH_3NH_3)_2TeCl_6$	University College London
73	Suraj Mahato	The influence of Al and Ga doping on the chemical and electrochemical cycling of T-$LiFeO_2$	University of Oxford
74	Daniel Martin	Scalability of Nb-based Anode Materials	Echion Technology
75	Kerry McMahon	Ferroelectric and Antiferroelectric Tetragonal Tungsten Bronzes for Ceramic Capacitor Applications	University of St Andrews
76	Holly McPhillips	Exploring the Unusual Magnetic Behaviour of $Mn_2Mo_3O_8$	University of Kent
77	Ashok Menon	Pushing the Limits of Operando X-ray Diffraction and Spectroscopy Studies for Industrial Li-ion batteries	University of Warwick
78	Ruby Morris	Phase transitions and compositional changes in Ca-Mg-H hydrogen storage systems	University of Glasgow
79	Michael J. Milton	Quantum Spin Liquids in Cation Ordered Perovskites	University of Edinburgh

80	Jing Ming	Dopant Clustering and Vacancy Ordering in Neodymium Doped Ceria	Queen Mary University of London
81	Liam Nagle-Cocco	Jahn-Teller behaviour in a layered nickel oxide with a triangular lattice	University of Cambridge
82	Jon Newnham	Synthesis of Layered Lead-Free Materials by Anion Substitution	University of Liverpool
83	Adair Nicolson	Investigating the impact of intrinsic defects on Cu_2SiSe_3 for PV applications	University College London
84	Bassey Oboho	Modelling Niobium based Solid Electrolytes for Lithium-ion Batteries	Loughborough University
85	Anthony Onwuli	Material design of quaternary sodium halide electrolytes	University of Liverpool
86	Jacob A Oyarzabal	Characterisation of Ceria and Ceria-Zirconia Materials Using Advanced Analytical Techniques	University of Warwick
87	Rory Powell	Atomic Layer vs. Sol-Gel Deposited Coatings for Long Cycle-Life Li-ion Battery Cathodes	University of Liverpool
88	Katie Pickering	The crystallisation and characterisation of basic magnesium chloride salts studied in situ using a laboratory SAXS/WAXS instrument.	University of Warwick
89	James Quirk	Design Principles for Grain Boundaries in Solid-State Lithium-Ion Conductor	University of Newcastle
90	Peng Ren	Structure and conductivity of $LiTa_2PO_8$ solid state electrolyte	Queen Mary University of London
91	George E. Rudman	Probing Ion Mobility in Fluorine-Doped Anti-Perovskite Solid Electrolytes	University of Durham
92	Alp E. Samli	A Computational Re-evaluation of Se as a Solar Absorber	University College London
93	Susan Schorr	Pitfalls in cation and anion mutation of quaternary chalcogenide semiconductors	Helmholtz-Zentrum Berlin für Materialien und Energie
94	Katie Scott	Discovery and property investigation of new intermetallic compounds	University of Liverpool
95	Struan Simpson	Searching for magnetoelectric coupling in the new cubic perovskite $CeBaMn_2O_6$	University of Warwick
96	Kieran Spooner	Discovery of the Novel Sustainable n-Type Thermoelectrics Zn_2NX (X = Cl, Br, I) by Anion Mutation of ZnO	University College London
97	Alex Squires	Computational design of high-entropy disordered rock salt cathode materials	University College London

98	James Steele	Bulk and Local Structural Evolution During Electrochemical Cycling in $NaNiO_2$	University of Cambridge
99	T. Wesley Surta	Chemical displacements drive the physical properties in a new Bi-based relaxorferroelectric system	University of Liverpool
100	Daniel Sykes	A Computational Study of the Intrinsic Defect Chemistry of Promising Sodium-Ion Cathode Material Na_2FePO_4F	University College London
101	Camilla Tacconis	High Voltage Cathode Materials for Next-Generation Magnesium Ion Batteries	University of Cambridge
102	Chris Thomas	Effect of flourine on the interfacial resistance in argyrodite based solid state batteries	University of Sheffield
103	Kasper Tolborg	Ab initio models of orientational disorder and phase transitions in hybrid piezoelectric materials	Imperial College London
104	Ben Tragheim	Interplay of Jahn-Teller distortions, orbital order and structural degrees of freedom in $LaMn_{1-x}Ga_xO_3$	University of Warwick
105	Xinwei Wang	Electron-lattice interaction in antimony chalcogenide semiconductors	Imperial College London
106	James Watt	LLZO outside of the glovebox – Carbonation of LLZO, its effect on electrical properties, and how to remove it	University of Sheffield
107	Joe Willis	Computational Prediction and Experimental Realisation of Earth-Abundant Transparent Conducting Oxide Ga-Doped $ZnSb_2O_6$	University College London
108	Jianwei Xu	Spark plasma sintering process for preparation of thermoelectric materials	AStar
109	Lin-Jie Yang	Manipulation of the optoelectronic properties of layered hybrid perovskites by molecular intercalation	University of St Andrews
110	Chumei Ye	The Thermal Properties of Hybrid Organic-Inorganic Perovskites (HOIPs)	University of Cambridge
111	Su-Hyun Yoo	Efficient electronic passivation schemes for surface calculations of semiconductors exhibiting spontaneous polarization	Imperial College London
112	Yao Yuan	Defect rocksalt structures in the La-Na-N system	University of Edinburgh

113	Michael Zambrano-Angulo	Characterization of the electronic and photovoltaics properties of zinc and silicon phthalocyanines with possible application to solar cells. Theoretical approach.	University College London
114	Fengchu Zhang	Orbital Orientation-based Theoretical Design of Single-Atom Catalysts for the Hydrogen Evolution Reaction	University College London
115	Xiaotian Zhang	Magnetoelectric coupling of rare-earth orthotantalates	University of Cambridge
116	Baiwen Zhao	Synthesis of mixed-metal cerium/zirconium UiO-66 and derived materials	University College London
117	Ying Zhou	Thermodynamics up to the melting point in a TaVCrW high entropy alloy: Systematic ab initio study aided by machine learning potentials	Loughborough University

List of Attendees

Isaac	Abrahams	Queen Mary University of London
Savya	Aggarwal	University College London
Jeremy	Allen	Royal Society of Chemistry
Sebastian	Altus	University of Sheffield
James	Annis	University of Warwick
Donna	Arnold	University of Kent
Alexander	Bell	Newcastle University; Durham University
Robert	Bell	University College London
Fiamma	Beradi	University of Cambridge
Prajna	Bhatt	University College London
Joshua	Bocarsly	University of Cambridge
Jan-Willem	Bos	Heriot-Watt University
Colm	Boyle	University of St Andrews
Joachim	Breternitz	Helmholtz-Zentrum Berlin für Materialien und Energie
Alexander	Browne	University of St Andrews
Johnathan	Bulled	University of Oxford
Hong	Cai	University of Liverpool
Javier	Castells-Gil	Universtiy of Birmingham
Celia	Castillo Blas	University of Cambridge
Jiayi	Cen	University College London
Xin	Chen	University of St Andrews
Ruiyong	Chen	University of Liverpool
Lucy	Clark	University of Birmingham
Chris	Collins	University of Liverpool
David	Cooke	University of Huddersfield
Lucia	Corti	University of Liverpool
Ana Carolina	Coutinho Dutra	Newcastle University
Jemma	Cox	Durham University
Mark	Crossman	University of Warwick
Yun	Dang	University of Liverpool
Luke	Daniels	University of Liverpool
James	Dawson	Newcastle University
Eliza	Dempsey	University of Edinburgh
Avishek	Dey	University College London
Seb	Dixon	Paragraf
Elias	Djafri	University of Kent
Patrick	Doheny	University of Kent
Tristan	Dolling	University Of Birmingham
Elizabeth	Driscoll	The University of Birmingham
Siân	Dutton	University of Cambridge
Matthew	Dyer	University of Liverpool
Matt	Edwards	University of Warwick
Stephen	Elliott	University of Cambridge
Tim	Evans	University College London
Ehsan	Ezzatpour Ghadim	University of Warwick

Viktoria	Falkowski	University of Oxford
Elisabeth	Fetter	University of Aberdeen
Nicolás	Flores-González	University of Glasgow
Frazer	Forrester	Newcastle University
Marina	Freitag	Newcastle University
Matthew	Friskey	University of St Andrews
Ben	Gade	University of St Andrews
Lavan	Ganeshkumar	University College London
Alexey	Ganin	University of Glasgow
Quinn	Gibson	University of Liverpool
Souvik	Giri	University of Oxford
Pooja	Goddard	Loughborough University
Naresh	Gollapally	University of Sheffield
Andrew	Goodwin	University of Oxford
Sam	Goodwin	University of Liverpool
Jennifer	Graham	ILL/ University of Birmingham
Ricardo	Grau-Crespo	University of Reading
Peter	Gross	University of Sheffield
Bastien Francesco	Grosso	University College London
Cara	Hawkins	University of Liverpool
Luisa	Herring Rodriguez	University College London
Craig	Hiley	University of Warwick
Yuri	Hirano	University of St Andrews
Thomas	Hitchings	University of Kent
Chun	Huang	Imperial College London
Ju	Huang	Imperial College London
Xuankai	Huang	Queen Mary University of London
Sophia	Hutton-Squire	University College London
Sean	Injac	University of Edinburgh
Teresa	Insinna	University of Cambridge
Katherine	Inzani	University of Nottingham
Saiful	Islam	University of Oxford
Sam	Ivko	University of Birmingham
Robert	Jackson	Keele University
Adam	Jackson	STFC
Chandrakant	Jadhav	University of Aberdeen
Xiaoyu	Jia	University College London
Pengcheng	Jing	University of Glasgow
Seán	Kavanagh	University College London, Imperial College London
Prakriti	Kayastha	Northumbria University
Nicola	Kelly	University of Oxford
John	Kilner	Imperial College London
Ayano	Kono	University of Cambridge
Gabriel	Krenzer	Imperial College London
Navaratnarajah	Kuganathan	Imperial College London

Evie	Ladbrook	University of Warwick
Roxanna	Lee	University College London
Zhenzhu	Li	Imperial College London
Yuhan	Liu	University College London
Hang	Liu	University of St Andrews
Suraj	Mahato	University of Oxford
Daniel	Martin	Echion Technologies
Xabier	Martinez de Irujo Labalde	University of Oxford
Lauren	McHugh	University of Liverpool
Kerry	McMahon	University of St Andrews
Holly	McPhillips	University of Kent
Emily	Meekel	University of Oxford
Ashok	Menon	University of Warwick
Michael	Milton	University of Edinburgh
Arianna	Minelli	University of Oxford
Jing	Ming	Queen Mary University of London
Ruby	Morris	University of Glasgow
Alexandra	Morscher	University of Liverpool
Irea	Mosquera Lois	Imperial College London
Otto	Mustonen	University of Birmingham
Liam	Nagle-Cocco	University of Cambridge
Jamie	Neilson	Colorado State University
Jon	Newnham	University of Liverpool
Thomas	Nicholas	University of Oxford
Adair	Nicolson	University College London
Anthony	Onwuli	Imperial College London
Kieran	Orr	University of Cambridge
Jacob	Oyarzabal	UNIVERSITY OF WARWICK
Galo	Paez Fajardo	University of Warwick
Robert	Palgrave	University College London
Julia	Payne	University of St Andrews
George	Phillips	University of Cambridge
Katie	Pickering	University of Warwick
Louis	Piper	University of Warwick
Rory	Powell	University of Liverpool
James	Quirk	Newcastle University
Peng	Ren	Queen Mary University of London
Alex	Rettie	University College London
George	Rudman	Durham University
Paul	Saines	University of Kent
Farheen	Sayed	University of Cambridge
Susan	Schorr	Helmholtz-Zentrum Berlin für Materialien und Energie
David	Scanlon	University College London
Katie	Scott	University of Liverpool
Mark	Senn	University of Warwick

Emily	Shaw	University of Cambridge
Yun	Shen	University College London
Yutong	Shen	University College London
Struan	Simpson	University of Warwick
Jan	Skakle	University of Aberdeen
Luke	Skilander	University of Liverpool
Stephen	Skinner	Imperial College London
Taylor	Sparks	University of Utah
Kieran B.	Spooner	University College London
Alex	Squires	University College London
Max	Stanzione	University of St Andrews
James	Steele	University of Cambridge
Wesley	Surta	University of Liverpool
Ady	Suwardi	IMRE, A*STAR
Daniel	Sykes	University College London
Camilla	Tacconis	University of Cambridge
Christopher	Thomas	University of Sheffield
Kasper	Tolborg	Imperial College London
Ben	Tragheim	University of Warwick
Aron	Walsh	Imperial College London
Richard	Walton	University of Warwick
Xinwei	Wang	Imperial College London
James	Watt	University of Sheffield
Dongsheng	Wen	University of Liverpool
Lucy	Whalley	Northumbria University
Joe	Willis	University College London
Grahame	Woollam	Novartis
Ruiqi	Wu	Imperial College London
Zixuan	Wu	Queen Mary University of London
Jianwei	Xu	Institute of Sustainability for Chemicals, Energy and Environment
Haixue	Yan	Queen Mary University of London
Linjie	Yang	University of St Andrews
Chumei	Ye	University of Cambridge
Su-Hyun	Yoo	Imperial College London
Yao	Yuan	University of Edinburgh
Fengchu	Zhang	University College London
Xiaotian	Zhang	University of Cambridge
Baiwen	Zhao	University of Warwick
Ying	Zhou	Loughborough University
Bonan	Zhu	University College London

Session One Abstracts

Monday 19th December, 2022

1.00 – 2.45 pm

Navigating Chemical Potential Landscapes for Synthetic Routes to Ternary Nitrides

James R Neilson,[1] Christopher L Rom[1].

[1] Department of Chemistry, Colorado State University, Fort Collins, CO, USA.

A significant challenge in materials chemistry is to rationally control composition and structure of materials to achieve desired properties. Unfortunately, metastability or glacial reaction kinetics limits the search for and synthesis of functional materials, particularly when it comes to nitride-based materials. Nitrides tend to be less thermodynamically stable than oxides, despite the significant cohesive energy of metal-nitrogen bonds. This cohesive energy also inhibits diffusion within and decomposition of nitrides, suggesting the need for high synthesis temperatures. While high synthesis temperatures would also be needed to overcome the barrier of N_2 dissociation, the entropy of gaseous N_2 at high temperatures leads to thermodynamic destabilization of nitrides. Therefore, alternative approaches are required. Here, we focus on the synthesis of $MgZrN_2$,[1] $CaZrN_2$, and $CaHfN_2$ enabled by navigating the chemical potential landscape provided from computational thermodynamics. *In situ* synchrotron X-ray diffraction provides mechanistic insight into the reaction pathway, thus allowing us to systematically revise synthesis reactions to obtain isolable material. Together, these studies illustrate the utility of examining the elemental chemical potentials at reaction interfaces to design reaction pathways that lead to the discovery of new materials.

References

[1] C. L. Rom, M. J. Fallon, A. Wustrow, A. L. Prieto, J. R. Neilson, *Chemistry of Materials*, 2021, **33**(13), 5345-5354.

Locating novel polyanionic cathode materials for Li-ion batteries in underexplored chemical spaces

Bonan Zhu,[1] Chris Pickard[2] and David Scanlon.[1]

[1] Department of Chemistry, University College London,

[2] Department of Materials Science and Metallurgy, University of Cambridge.

Low-cost, highly scalable batteries are crucial for grid-storage that underpins the wide-adoption of sustainable energy. Historically, the discovery of cathodes materials had led to significant advances in the field of Li-ion batteries. Coming up with new cathode systems is an experimentally challenging task, which can be accelerated by via computational searches. Polyanion-based materials, such as $LiFePO_4$, typically have lower theoretical capacities than their oxide-based counterparts, yet the richness in charge and geometry among different polyanions allows tuning key cathode parameters through structural-property relationships. Higher capacities are achievable if multi-electron redox (such as in ε-VOPO4e) or anionic redox can be incorporated. We have developed procedures for mining polyanionic units from databases of inorganic structures, and subsequently evaluating their potential as building blocks for cathode materials. The focus on unexplored chemical spaces mean traditional database-centric structure prediction approaches are less applicable. Instead, *ab initio* random structure searching (AIRSS)[2–5] is employed to locate the lower energy structures in underexplored chemical spaces from only the desired compositions and polyanion units as the inputs. Having a comprehensive table of all known polyanions would also benefit other field of solid-state materials beyond batteries.

References

[1] Siu, C.; Seymour, I. D.; Britto, S.; Zhang, H.; Rana, J.; Feng, J.; Omenya, F. O.; Zhou, H.; Chernova, N. A.; Zhou, G.; Grey, C. P.; Piper, L. F. J.; Whittingham, M. S. Enabling Multi-Electron Reaction of ε-VOPO4 to Reach Theoretical Capacity for Lithium-Ion Batteries. *Chem. Commun.* **2018**, *54* (56), 7802–7805.

[2] Pickard, C. J.; Needs, R. J. Ab Initio Random Structure Searching. *Journal of physics. Condensed matter : an Institute of Physics journal* **2011**, *23* (5), 053201–053201

[3] Lu, Z.; Zhu, B.; Shires, B. W. B.; Scanlon, D. O.; Pickard, C. J. Ab Initio Random Structure Searching for Battery Cathode Materials. *J. Chem. Phys.* **2021**, *154* (17), 174111.

[4] Zhu, B.; Scanlon, D. O. Predicting Lithium Iron Oxysulfides for Battery Cathodes. *ACS Appl. Energy Mater.* **2022**, *5* (1), 575–584. https://doi.org/10.1021/acsaem.1c03094.

[5] Zhu, B.; Lu, Z.; Pickard, C. J.; Scanlon, D. O. Accelerating Cathode Material Discovery through Ab Initio Random Structure Searching. *APL Materials* **2021**, *9* (12), 121111.

Photocatalytic and Photocurrent Responses to Visible Light of the Lone-Pair-Based Oxysulfide $Sr_6Cd_2Sb_6S_{10}O_7$

Sandy AL Bacha,[1,2,3] Sébastien Saitzek,[1] Emma McCabe[3] and Houria Kabbour.[1]

[1] Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France,

[2] University of Kent, School of Physical Sciences, Canterbury, Kent CT2 7NH, U.K,

[3] Durham University, Departement of Physics, Durham DH1 3LE, U.K.

For sustainable hydrogen production, numerous materials such as oxides and sulfides have been found to be potential photocatalysts for water splitting. One effective design strategy for a successful photocatalytic reaction under visible light is anionic substitution.[1] Several oxysulfides have been recently highlighted in this field, for example $Y_2Ti_2O_2S_5$ which was stable and gave stoichiometric production of O_2 and H_2 under visible light.[2] Another important design strategy for an improved photocatalytic activity is to introduce a heteroleptic cation coordination environment, beneficial to enhance polarity and electron-hole separation.[3,4]

We present a combined experimental (photoconduction, photocatalysis) and computational (electronic band structure, fat bands, charge carries' effective masses) study on the recently reported polar oxysulfide $Sr_6Cd_2Sb_6S_{10}O_7$,[5] which contains three different Sb^{3+} $5s^2$ cation-containing units: SbO_3, SbS_5 (homoleptic) and $SbOS_4$ (heteroleptic one) (**Figure 1a**).

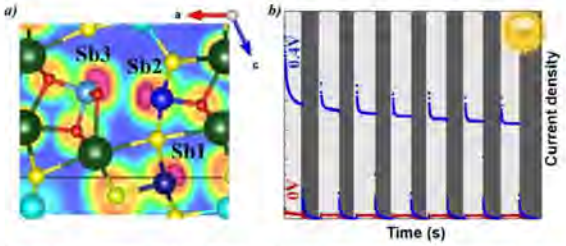


Figure 1: *(a)* DFT-computed ELF for Sb^{3+}, *(b)* Photocurrent response under sunlight.

Our spectroscopy and photocurrent measurements indicate the potential of $Sr_6Cd_2Sb_6S_{10}O_7$ for photocatalytic applications with efficient electron-hole separation upon illumination (**Figure 1b**).[6] Theoretical calculations give a comprehensive analysis on the Sb^{3+} $5s^2$ lone pair activity. Our comprehensive investigation into $Sr_6Cd_2Sb_6S_{10}O_7$ reveals the roles of its polar structure, polar Sb^{3+} coordination environments and the $5s^2$ lone pair in making this compound a potential candidate for solar water splitting photocatalysis.[6]

References

[1] H. Kageyama, K. Hayashi, K. Maeda, J.P. Attfield, Z. Hiroi, J.M. Rondinelli and K.R. Poeppelmeier, *Nat. Commun*, 2019, **9(772)**, 1-15.
[2] Q. Wang, M. Nakabayashi, T. Hisatomi, S. Sun, S. Akiyama, Z. Wang, Z. Pan, X. Xiao, T. Watanabe, T. Yamada, *Nat. Mater.* 2019, **18 (8)**, 827-832.
[3] N. Vonrüti, U. Aschauer, *Journal of Materials Chemistry A*, 2019, **7(26)**, 15741-15748.
[4] N. Vonrüti, U. Aschauer, *The Journal of Chemical Physics*, 2020, **152(2)**, 024701.
[5] R. Wang, Fei.Liang, F. Wang, Y. Guo, X. Zhang, Y. Xiao, K. Bu, Z. Lin, J. Yao and T. Zhai, *Angewandte Chemie International Edition*, 2019, **58(24)**, 8078-8081.
[6] S. AL Bacha, S. Saitzek, E.E. McCabe, H. Kabbour, *Inorganic Chemistry*, 2022.

Revenge of the .cif: incorporating structural distance metrics into the DiSCoVeR algorithm

Taylor D. Sparks,[1,2] Sterling G. Baird,[1] Michael Moran,[2,3] Michael Gaultois,[2,3]
and Matt Rosseinsky[2,3]

[1] University of Utah, Materials Science & Engineering Department

[2] University of Liverpool, Chemistry Department

[3] Leverhulme Research Centre for Functional Materials Design, University of Liverpool

Machine learning already enables the discovery of new materials by providing rapid predictions of properties to complement slower calculations and experiments. However, a persistent criticism of machine learning enabled materials discovery is that new materials are very similar, both chemically and structurally, to previously known materials. This begs the question “Can generative machine learning ever learn new chemistries and families of materials that differ from those present in the training data?” In this talk, I will describe the Descending from Stochastic Clustering Variance Regression (DiSCoVeR) algorithm. In its original implementation,[1] the DiSCoVeR algorithm utilized the Element Movers Distance (ElMD)[2] as a powerful new metric of chemical similarity. Using ElMD along with density-aware dimensionality reduction, clustering, and a regression model, the DiSCoVeR algorithm could steer materials discovery towards novel chemistries. Recently, we have developed several new metrics for structural similarity such as SiteNET+Deep InfoMax[3] or crystal graph distances[4] and incorporated these into the DiSCoVeR algorithm allowing researchers to prioritize chemical, structural, or combination novelty.

References

[1] S. G. Baird, T. Q. Diep, and T. D. Sparks. "DiSCoVeR: a materials discovery screening tool for high performance, unique chemical compositions." *Digital Discovery*, 2022, **1**, 226-240.

[2] C. Hargreaves, M. S. Dyer, M. W. Gaultois, V. A. Kurlin, M. J. Rosseinsky "The earth mover’s distance as a metric for the space of inorganic compositions." *Chemistry of Materials*, 2020, **32**(24), 10610-10620.

[3] M. Moran, M. W. Gaultois, V. V. Gusev, and M. J. Rosseinsky, “Site-Net: Using global self-attention and real-space supercells to capture long-range interactions in crystal structures.” *arXiv* 2022.

[4] D. Widdowson, M. M. Mosca, A. Pulido, A. I. Cooper, and V. Kurlin, “Average Minimum Distances of Periodic Point Sets-Foundational Invariants for Mapping Periodic Crystals.” *MATCH-COMMUNICATIONS IN MATHEMATICAL AND IN COMPUTER CHEMISTRY*, 2022, **87**(3), 529-559.

Session Two

Abstracts

Monday 19th December, 2022

3.30 – 5.00 pm

Synthesis of faceted pristine and Mg-doped single-crystal LNO cathode materials and its electrochemical study

Naresh Gollapally,[1] Samuel Booth[1], Laura J Wheatcroft[1], Edmund J. Cussen[1], Serena A. Cussen[1]*

[1] Department of Materials Science and Engineering, University of Sheffield, Sir Robert Hadfield Building, Sheffield, S1 3JD, UK

High energy nickel (Ni)-rich layered oxide such as $LiNiO_2$ (LNO) cathode materials will play a key role in advanced lithium-ion batteries, but it suffers with electro-mechanical degradation, parasitic reactions, and gas evolution[1]. Electro-mechanical degradation is usually seen in polycrystalline battery materials which consist of nano-sized primary particles. The anisotropic volume change during charge/discharge process leads to the fracture in polycrystalline materials and that results dramatically increases particle surface area, aggravating surface-related degradations including surface phase transformation, transition metal dissolution, lattice oxygen release, electrolyte decomposition, rapid impedance growth and capacity decay[2,3]. So, the single-crystalline Ni-rich cathodes have a great potential to address the above-mentioned challenges present in its polycrystalline counterpart. We have synthesized faceted single crystal LNO materials via flux assisted co-precipitation method. These single-crystal LNO shown comparable initial discharge capacity and better capacity retention than its counter polycrystalline material. Moreover, the Mg-doped single crystal LNO has retained its faceted morphology. Crack resistant single-crystal layered oxides discloses an alternate way to develop better battery cathode materials, beyond the traditional polycrystalline materials.

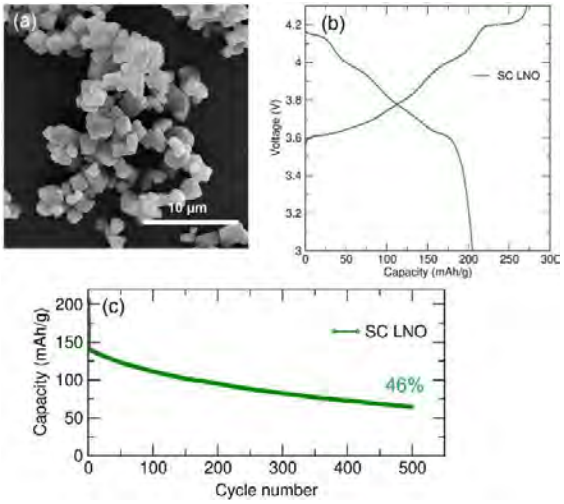


Fig. 1 SEM image (a), first charge-discharge profile (b) and capacity retention of single crystal $LiNiO_2$

References

[1] G. E. Blomgren, The development and future of lithium ion batteries. *J. Electrochem. Soc.* 2017, **164**, A5019−A5025.

[2] G. Qian, Y. Zhang, L. Li, R. Zhang, J. Xu, Z. Cheng, S. Xie, H. Wang, Q. Rao, Y. He, Y. Shen, L. Chen, M. Tang, Z-F. Ma, Single-crystal nickel-rich layered-oxide battery cathode materials: synthesis, electrochemistry and intra-granular fracture. *Energy Storage Mater.* 2020, **27**, 140-149.

[3] Y. Bi, J. Tao, Y. Wu, L. Li, Y. Xu, E. Hu, B. Wu, J. Hu, C. Wang, J-G. Zhang, Y. Qi, J. Xiao, Reversible planar gliding and microcracking in a single-crystalline Ni-rich cathode. *Science*, 2020, **370**, 1313–1317

Synthesis-Dependent Structure-Property Relationships of Quantum Materials

J. N. Graham,[1,2] J. R. Stewart,[3] J. A. Cooley,[4] M. Songvilay,[5] G. Confalonieri,[6]

A. D. Fortes,[3] P. Manual,[3] A. R. Wildes[2] and Lucy Clark.[1]

[1] School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK,

[2] Institut Laue-Langevin, 71 Avenue des Martyrs, 38000 Grenoble, France,

[3] ISIS Facility, Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11, 0QX, UK,

[4] Department of Chemistry and Biochemistry, California State University Fullerton,
Fullerton, California 92834-6866, USA,

[5] Institut Néel, CNRS and Université Grenoble Alpes, 38000 Grenoble, France,

[6] ESRF, 71 Avenue des Martyrs, 38000 Grenoble, France.

Quantum ($S \leq 1$) magnets with frustrated magnetic interactions are predicted to give rise to a rich variety of exotic quantum materials properties.[1] This includes novel quasiparticle excitations that could be manipulated to pave the way to a new form of topologically-protected quantum computing.[1] However, the complexity of quantum materials often makes characterising the exact nature of their exotic properties extremely challenging. For instance, in frustrated quantum magnets, the degeneracy of possible magnetic ground states stemming from the competition of magnetic interactions means that the experimentally observed properties are extremely sensitive to any defects or disorder in the underlying materials structure, which can vary from sample to sample depending on the synthesis method used.[2,3] This in turn poses challenges for the development of our theoretical understanding of quantum materials, and ultimately limits our current ability to design and synthesise new quantum materials with properties tailored towards specific applications.[4]

In this talk, I will discuss our recent efforts to explore the synthesis-structure-property relationships of the frustrated $S = ½$ spinel, ZnV_2O_4. Previous studies of this material—which contains a pyrochlore network of antiferromagnetically coupled V^{3+} ions—reveal that the structural and magnetic ground states are sample dependent, ranging from a tetragonally-distorted classical antiferromagnet to a cubic and highly frustrated spin glass.[5-9] I will present two samples of ZnV_2O_4, one prepared via a conventional solid-state synthesis method and the other via a novel rapid microwave-assisted route. I will show how these two different synthesis routes distinctly impact the evolution of the chemical and magnetic behaviour of ZnV_2O_4 through a combination of high-resolution powder neutron and synchrotron X-ray diffraction, magnetometry, and X-ray PDF and diffuse neutron scattering measurements. I doing so, I will demonstrate the potential for rapid microwave-assisted synthesis as an appealing high-throughput approach to high-quality inorganic quantum materials discovery.

References

[1] C. Broholm *et al.*, *Science*, 2020, **367**, 6475.
[2] D. F. Bowman *et al.*, *Nat. Commun.*, 2019, **10**, 637.
[3] K. Tustain *et al.*, *Chem. Mater.*, 2021, **33**, 9638.
[4] D. N. Basov *et al.*, *Nat. Mater.*, 2017, **16**, 1077.
[5] Y. Ueda *et al.*, *J. Phys. Soc. Jpn.*, 1997, **66**, 778.
[6] M. Reehuis *et al.*, *Eur. Phys. J. B*, 2003, **35**, 311.
[7] S. Ebbinghaus *et al.*, *J. Alloys Compd.*, 2004, **370**, 75.
[8] A. J. Browne and J. P. Attfield, *Phys. Rev. B*, 2020, **101**, 024112.

Truchet-tile structure of a topologically aperiodic metal-organic framework

Emily G. Meekel,[1] Ella M. Schmidt,[1,2] Lisa J. Cameron,[3] A. David Dharma,[3] Hunter J. Windsor,[3] Samuel G. Duyker,[3,4] Arianna Minelli,[1] Tom Pope,[5] Giovanni Orazio Lepore,[6] Ben Slater,[5] Cameron Kepert,[3] and Andrew L. Goodwin[1,*]

[1]Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, UK
[2]Fachbereich Geowissenschaften, Universität Bremen, D-28359 Bremen, Germany
[3]School of Chemistry, University of Sydney, NSW 2006, Australia
[4]Sydney Analytical, Core Research Facilities, University of Sydney, NSW 2006, Australia
[5]Department of Chemistry, University College London, London WC1H 0AJ, UK
[6]Earth Sciences Department, University of Florence, Florence 50121, Italy

Periodic tilings can store information if individual tiles are decorated to lower their symmetry. Truchet tilings—the broad family of space-filling arrangements of such tiles—offer an efficient mechanism of visual data storage related to that used in barcodes and QR codes[1,2]. Here, we show that the crystalline metal–organic framework $[\mathrm{OZn_4}][1,3\text{-benzenedicarboxylate}]_3$, or TRUMOF-1, is an atomic-scale realisation of a complex three-dimensional Truchet tiling. Its crystal structure consists of a periodically arranged assembly of identical zinc-containing clusters connected uniformly in a well-defined but disordered fashion to give a topologically aperiodic microporous network (Fig. 1). We suggest that this unusual structure emerges as a consequence of geometric frustration in the chemical building units from which it is assembled.

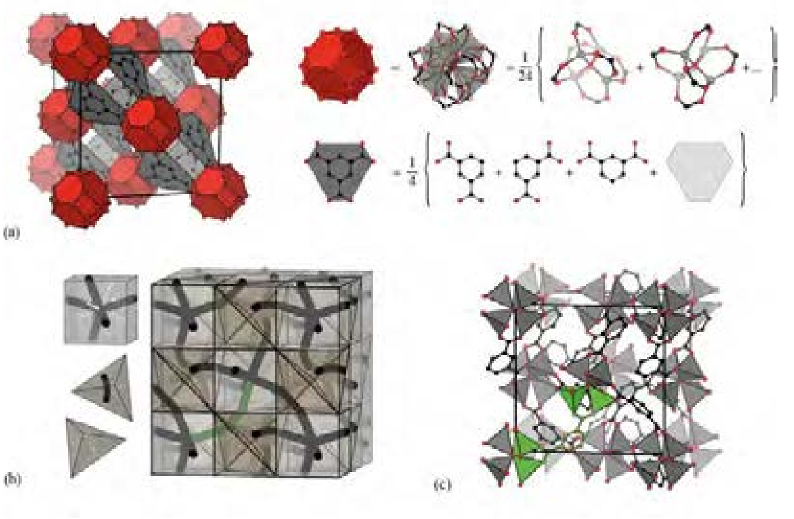


Figure 1. Crystal structure of TRUMOF-1: a) Representation of the average structure of TRUMOF-1 with $\mathrm{OZn_4}$-centred polyhedra shown as red cuboctahedra and trigonally-symmetric ligand sites shown as grey triangles, with breakdown of local configurations of the average metal cluster and linker site. b) The Truchet tiles used in our mapping, which correspond to (top–bottom) the pseudo-octahedral inorganic cluster orientations, the 1,3-bdc linker orientations, and the positions of ligand vacancies. c) One possible 1 x 1 x 1 approximant of the TRUMOF-1 structure with atom coordinates and cell geometry optimised using DFT.

References

[1] S. Truchet, *Mem. Acad. R. Sci. Paris*, 1704, 363-372.

[1] C. S. Smith, *Leonardo,* 1987, **20**, 373-385.

Control of ionic conductivity by lithium distribution in the cubic oxide argyrodites $Li_{6+x}P_{1-x}Si_xO_5Cl$

Alexandra Morscher,[1] Benjamin B. Duff,[1,2] Guopeng Han,[1] Luke M. Daniels,[1] Yun Dang,[1] Marco Zanell,[1] Manel Sonni,[1] Ahmad Malik,[1] Matthew S. Dyer,[1] Ruiyong Chen,[1] Frederic Blanc,[1,2] John B. Claridge[1] and Matthew J. Rosseinsky.[1]

[1] Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD Liverpool, UK
[2] Stephenson Institute for Renewable Energy, University of Liverpool, Peach Street, L69 7ZF Liverpool, UK

All Solid-State Batteries are of considerable interest since they have potential for increased battery safety and energy density.[1] Sulphide argyrodite materials demonstrate superionic conductivity but they suffer from stability issues that could be addressed by oxide argyrodites.[2] Despite this, very few oxide argyrodites have been reported due to their low ionic conductivities (10^{-9} S cm^{-1}).[3]

We present the discovery of a new oxide argyrodite in the Li-Si-P-O-Cl phase field which exhibits an ionic conductivity of $1.82(1) \times 10^{-6}$ S cm^{-1}, an increase of three orders of magnitude compared to existing oxide argyrodites (Figure 1a). The enhanced transport properties result from the stabilisation of Li site disorder to room temperature as well as the occupancy of additional interstitial Li sites (T5/T5a/T4/T3) (Figure 1b). This gives rise to a unique Li sublattice which we characterise via X-ray diffraction. The material exhibits increased air stability compared to sulphide analogues.

The ability to enhance ionic conductivity through control at the structural and compositional level highlights the advances that can be made in the largely unexplored field of oxide argyrodites.

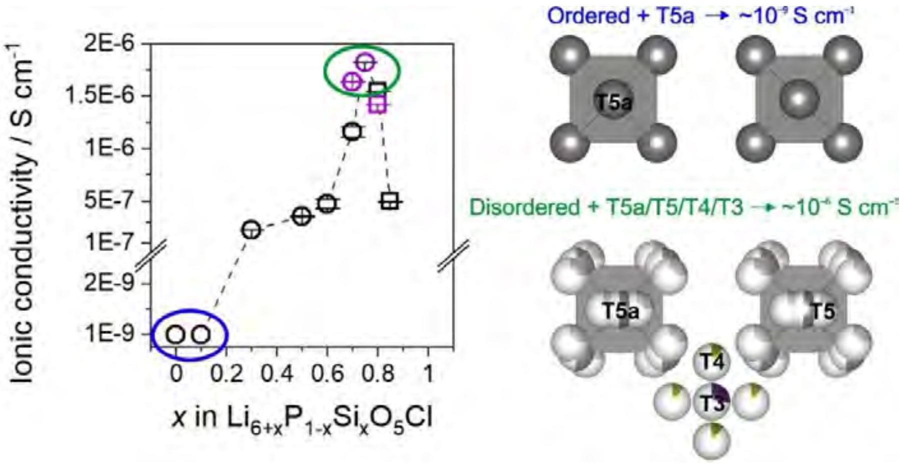


Figure 1: a) Room temperature ionic conductivity as a function of x in $Li_{6+x}P_{1-x}Si_xO_5Cl$; b) Highlighting the effect of additional Li sites (T5/T5a/T4/T3) and disorder on the ionic conductivity in $Li_{6+x}P_{1-x}Si_xO_5Cl$

References

[1] J. Janek, W.G. Zeier, *Nature Energy*, 2016, **1(9)**, 1-4.

[2] H.J. Deiseroth, S.T. Kong, H. Eckert, J. Vannahme, C. Reiner, T. Zaiß, T. and M. Schlosser, *Angewandte Chemie International Edition*, 2008, ***47*(4)**, 755-758.

[3] S.T. Kong, H.J. Deiseroth, *Zeitschrift für anorganische und allgemeine Chemie*, 2010, ***636*(11)**, 2115-2115.

Formation of new crystalline qtz-[Zn(mIm)$_2$] polymorph from amorphous ZIF-8

Celia Castillo-Blas,[1] Michael F. Thorne,[1] Lauren N. McHugh,[1] Adam F. Sapnik,[1] Chloe S. Coates,2
Farheen N. Sayed,[2] Clare P. Grey,[2] David A. Keen,[3] Ivan da Silva,[3] Krunoslav Užarević,[4] and
Thomas D. Bennett,[1]

[1] Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UK

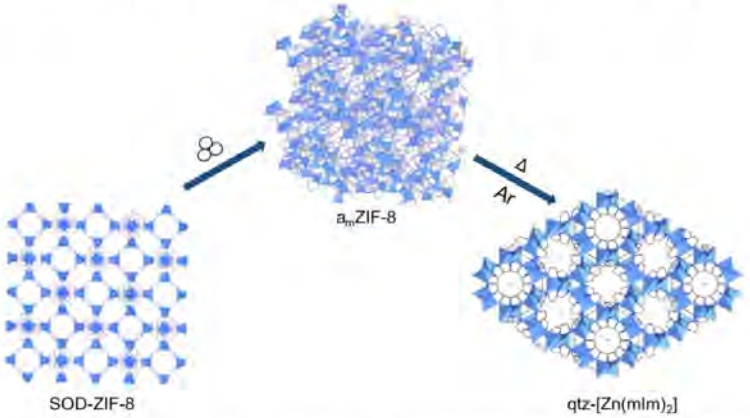
[2] Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge, UK

[3] ISIS Facility, Rutherford Appleton Laboratory, Harwell Campus, Didcot, Oxfordshire, UK

[4]Ruđer Bošković Institute, Bijenička Cesta 54, Zagreb, HR-10000, Croatia

Zeolitic imidazolate frameworks (ZIFs) are of immense interest within materials science due to their promising applications in gas storage and separation, catalysis and drug delivery. ZIFs are a subclass of hybrid porous crystalline materials known as metal-organic frameworks (MOFs). They are formed from the self-assembly of tetrahedrally-coordinated transition metals and an imidazolate linker. Thanks to its facile-synthesis, high thermal stability and great surface area, the most well-studied ZIFs is ZIF-8 [Zn(MIm)$_2$] (MIm = 2-methylimidazolate), with a sodalite (SOD) topology. This material has been related to more of 5,600 publications and it is commercially available.

Recently, amorphous and glassy ZIFs have gained great attention thanks to their utility in drug delivery, gas separation and ion transportation. These amorphous phases retain the basic building blocks and connectivity of their crystalline parents. However, thermal characterisation of these materials still remains extremely poor. Here we study the structural transition of the mechanically amorphised ZIF-8 upon heating, which exhibited a recrystallisation process. We also deciphered the structure of a new topology of ZIF-8, qtz-[Zn(MIm)$_2$] using charge flipping approach from powder diffraction and also compare CO$_2$ and dye absorption of the three polymorphs (sodalite, amorphous and quarzt), demonstrating that we can form unprecedented phases from amorphous MOFs.



Scheme 1. Schematic representation of the synthetic procedure of qtz-[Zn(MIm)$_2$] showing the three different polymorphs involved.

References

[1] M.F. Thorne, C. Castillo-Blas, L. N. McHugh, A. M. Bumstead, G. Robertson, A. F. Sapnik, C. S. Coates, F. N. Sayed, C. P. Grey, D. A. Keen, M. Etter, I. da Silva, K. Užarević, and T. D. Bennett *Chem. Commun*., 2022,**58**, 11949-11952.

Session Three Abstracts

Tuesday 20th December, 2022

9.00 – 10.30 am

Grain Boundary Chemistry in Mixed Conducting Oxides

John Kilner
Department of Materials
Imperial College London
London SW7 2AZ
j.kilner@imperial.ac.uk

The development of materials for solid oxide electrochemical devices has been a topic of interest for a number of decades. In particular, the use of porous ceramic Mixed Ionic Electronic Conductors (MIECs) for use as electrodes has been pursued because of their excellent performance as air electrodes in solid oxide cells. A typical example is the mixed conducting perovskite oxide $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ (LSCF6428) , where the oxygen diffusivity approaches 10^{-18}cm^{2}s^{-1} at 750°C, as shown in Figure 1 [1]. As the technology has progressed, there has been a desire to lower the temperature of operation, which in early devices was as high as 1000°C, down to 700°C and more recently 5-600°C and below. As the operation temperatures reduce the transport of oxygen ions in the lattice drops to levels where it is no longer enough to give satisfactory performance as an electrode. This has led to the concept that oxygen transport along interfaces, both homogenous [2-4] and heterogeneous [5], can be promoted to give a suitable net oxygen transport.

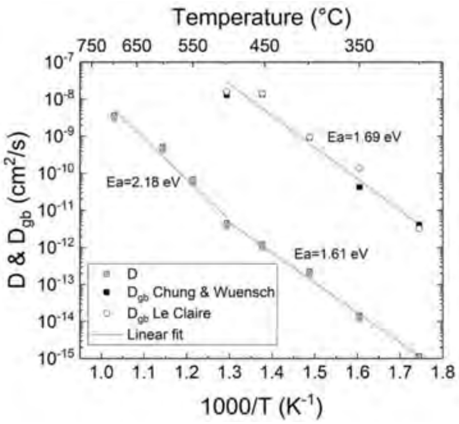


Figure 1 Bulk and Grain Boundary oxygen transport for LSCF6428

For MIEC materials, gaining an understanding of the grain boundary transport of oxygen is key to developing ideas of grain boundary engineering to enhance performance at the lower temperatures. This contribution will cover some of the recent progress that has been made in understanding the grain boundary chemistry of these complex oxide materials and the effect that this can have on the transport of oxygen.

[1] V. Thoreton, M. Niania, J. Druce, H. Tellez, J.A. Kilner, *Journal Of The Electrochemical Society* **169** (2022) (4).
[2] A.M. Saranya, A. Morata, D. Pla, M. Burriel, F. Chiabrera, I. Garbayo, A. Hornes, J.A. Kilner, A. Tarancon, *Chemistry of Materials* **30** (2018) (16) 5621.
[3] A.M. Saranya, D. Pla, A. Morata, A. Cavallaro, J. Canales-Vázquez, J.A. Kilner, M. Burriel, A. Tarancón, *Advanced Energy Materials* **5** (2015) (11) 1500377.
[4] E. Navickas, T.M. Huber, Y. Chen, W. Hetaba, G. Holzlechner, G. Rupp, M. Stoger-Pollach, G. Friedbacher, H. Hutter, B. Yildiz, J. Fleig, *Physical Chemistry Chemical Physics* **17** (2015) (12) 7659.
[5] S.M. Yang, S. Lee, J. Jian, W. Zhang, P. Lu, Q. Jia, H. Wang, T. Won Noh, S.V. Kalinin, J.L. MacManus-Driscoll, *Nature Communications* **6** (2015) (1) 8588.

Evidence for a disorder-induced spin liquid in the tuneable spin ladder-chain system $Ba_2CuTe_{1-x}W_xO_6$

Otto Mustonen,[1,2] Charlotte Pughe,[2] Alexandra Gibbs,[3,4,5] Alexander Yaresko,[5] Peter Baker,[4] Lucile Mangin-Thro,[6] Helen Walker[4] and Edmund Cussen.[2]

[1] University of Birmingham, [2] University of Sheffield, [3] University of St Andrews, [4] ISIS Neutron and Muon Source, [5] Max Planck Institute for Solid State Research, [6] Institut Laue-Langevin.

Exotic quantum states can emerge in magnetic materials with $S = 1/2$ quantum spins and low-dimensional interactions. An important class of such materials are spin liquids: materials that do not magnetically order or freeze even at absolute zero.[1] Spin liquids have unusual magnetic excitations that could be used as the building blocks of next-generation quantum computers. The ideal spin liquid candidate has been seen as structurally perfectly ordered. However, recent theoretical and experimental studies show that structural disorder can stabilise a spin liquid phase in some systems. The double perovskite $Sr_2CuTe_{1-x}W_xO_6$ with a square lattice of Cu^{2+} ($S = 1/2$) cations is a leading candidate for a disorder-induced spin liquid.[2] Replacing the d^{10} Te^{6+} cation with a d^0 W^{6+} cation enables the tuning of magnetic interactions due to an orbital hybridization effect.

Here we use the same d^{10}/d^0 approach to tune magnetism in the hexagonal perovskite system $Ba_2CuTe_{1-x}W_xO_6$. The crystal structure consists of corner-sharing perovskite-type layers and face-sharing CuO_6-TeO_6-CuO_6 trimers. Importantly, the Cu^{2+} cations in the perovskite-layer form a spin ladder. Our neutron and synchrotron X-ray diffraction data show that W^{6+} is almost exclusively doped into the perovskite-layer.[3] This allows for direct tuning of magnetic interactions in a spin ladder for the first time. Magnetic susceptibility fitting and density functional theory calculations show that $Ba_2CuTe_{1-x}W_xO_6$ changes from a spin ladder to a zig-zag spin chain with increasing x. Muon spectroscopy reveals the complete suppression of magnetic order upon doping supporting a spin liquid state. Inelastic neutron scattering experiments rule out a gapped spin singlet state.

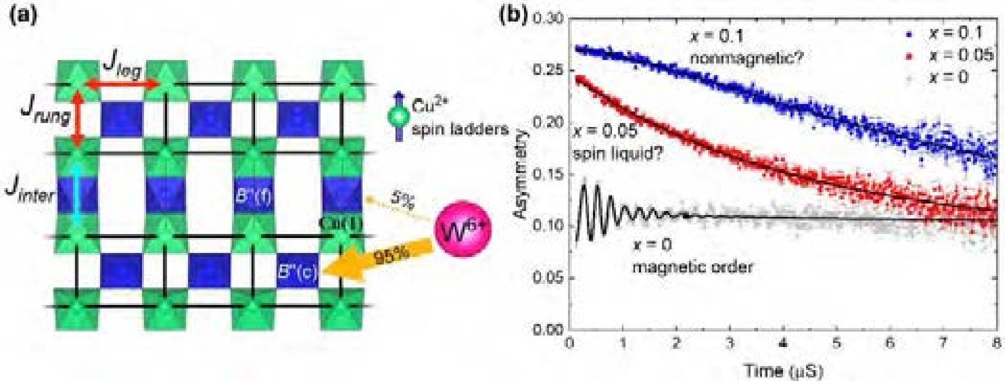


Figure 1. (a) The spin ladder in $Ba_2CuTe_{1-x}W_xO_6$ is formed by the Cu^{2+} ($S = 1/2$) cations in green. Of the two Te-sites in blue, W is almost exclusively doped onto the corner-sharing B''(c) site. This allows direct tuning of interactions in the spin ladder. (b) Muon spectroscopy data revealing significant differences between the $x = 0$, 0.05 and 0.1 samples. The parent phase $x = 0$ is magnetically ordered, whereas the doped samples do not order. The $x = 0.05$ sample behaves like a spin liquid.

References

[1] L. Balents, *Nature*, 2010, **464**, 199–208.
[2] O. Mustonen *et al.*, *Nat. Commun.*, 2018, **9**, 1085.
[3] C. Pughe, O. H. J. Mustonen *et al.*, *Inorg. Chem.*, 2022, **61**, 4033–4045.

Disentangling Cation and Anion Dynamics in Li_3PS_4 Solid Electrolytes

Frazer N. Forrester,[1] James A. Quirk,[1] Theo Famprikis[2] and James A. Dawson.[1,3]

[1] Chemistry- School of Natural and Environmental Sciences, Newcastle University,
Newcastle upon Tyne, NE1 7RU, UK
[2] Department of Radiation Science and Technology, Faculty of Applied Sciences, Delft
University of Technology, 2629JB Delft, The Netherlands
[3] Centre for Energy, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK.

A prerequisite for the realization of solid-state batteries is the development of highly conductive solid electrolytes. Li_3PS_4 is the archetypal member of the highly promising thiophosphate family of Li-ion conductors. Despite a multitude of investigations into this material, the underlying atomic-scale features governing the roles of and the relationships between cation and anion dynamics, in its various temperature-dependent phases, are yet to be fully resolved. On this basis, we provide a comprehensive molecular dynamics study to probe the fundamental mechanisms underpinning fast Li-ion diffusion in this important solid electrolyte material. We first determine the Li-ion diffusion coefficients and corresponding activation energies in the temperature-dependent γ-, β- and α-phases of Li_3PS_4 and relate them to the structural and chemical characteristics of each polymorph. The roles that both cation correlation and anion libration play in enhancing the Li-ion dynamics in Li_3PS_4 are then isolated and revealed. For γ- and β-Li_3PS_4, our simulations confirm that interatomic Li–Li separation is pivotal in determining (and restricting) their Li-ion diffusion. For α-Li_3PS_4, we quantify the significant role of Li–Li correlation and anion dynamics in dominating Li-ion transport in this polymorph for the first time. The fundamental understanding and analysis presented is expected to be highly applicable to other solid electrolytes where the interplay between cation and anion dynamics is crucial to enhancing ion transport.

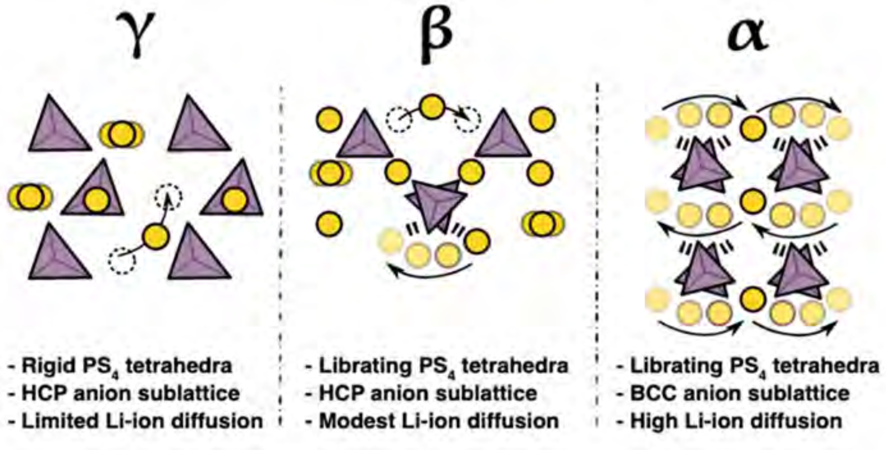


Figure 1. Schematic depicting the main structural and dynamic properties responsible for the different magnitudes of Li-ion transport in γ-, β- and α-Li_3PS_4.

References

F.N. Forrester, J.A. Quirk, T, Famprikis and J.A. Dawson, *Chem. Mater*, 2022. *(Just accepted)*

Electronic and Thermal Transport Descriptors in Thermoelectrics

Ady Suwardi,[1] and Jianwei Xu.[2]

[1] Institute of Materials Research and Engineering, 2 Fusionopolis Way, 138634 Singapore,

[2] Institute of Sustainability for Chemicals, Energy and Environment, Agency for Science, Technology and Research (A*STAR), Singapore 627833.

Thermoelectrics is attractive as a green and sustainable way for harnessing waste heat and cooling applications. Designing high performance thermoelectrics involves navigating the complex interplay between electronic and heat transports. This fundamentally involves understanding the scattering physics of both electrons and phonons, as well as maximizing symmetry-breaking in entropy and electronic transports. In the last two decades, thermoelectrics have progressed in leaps and bounds thanks to parallel advancements in scientific technologies and physical understandings. Figure of merit zT of 2 and above have been consistently reported in various materials, especially Chalcogenides.

In this talk, a broad picture of physically driven optimization strategies for thermoelectric materials will be discussed, with emphasis on electronic transport aspect of inorganic materials.[1] In addition, the effect of nanostructuring and low dimensional materials as independent tuning knob to enhance thermoelectric properties will be emphasized. Furthermore, various newly coined metrics such as quality factors, electronics quality factor, electronic fitness function, weighted mobility, and Fermi surface complexity factor. More importantly, the non-trivial interdependencies between various physical parameters even at a very fundamental level will be elaborated.[1]

With the physical understanding in mind, we discuss the outlook for the device oriented research as well as commercial applications in thermoelectrics. Specific example on recycling/upcycling silicon from solar cells into thermoelectrics will be presented.[2] The intuition derived from this talk will be useful for understanding the thermal and electronic transports in inorganic materials.

References

1. Jia N, Cao J, Tan XY, Dong J, Liu H, Tan CK, Xu J, Yan Q, Loh XJ, Suwardi A. Thermoelectric materials and transport physics. *Materials Today Physics*. 2021 Nov 1;21:100519.
2. Cao J, Sim Y, Tan XY, Zheng J, Chien SW, Jia N, Chen K, Tay YB, Dong JF, Yang L, Ng HK. Upcycling Silicon Photovoltaic Waste into Thermoelectrics. *Advanced Materials*. 2022 May;34(19):2110518.

Session Four Abstracts

Tuesday 20th December, 2022

11.15 am - 1.00 pm

Steric Engineering of point defects in lead halide perovskites

Dr Lucy Whalley[1]

[1] Department of Mathematics, Physics and Electrical Engineering, Northumbria University, Newcastle Upon Tyne, NE1 8ST, United Kingdom.

Organic-inorganic lead halide perovskites (OLHPs) have attracted wide interest for their application in optoelectronics. Single junction halide perovskite solar cells now exceed 25% power conversion efficiency,[1] with the most stable and efficient devices employing mixed organic (methylammonium, MA and formamidinium, FA) or inorganic (Cs, Rb) cations on the A-site of the ABX_3 perovskite structure. A-site cation engineering is primarily used to improve thermal and chemical stability;[2] the impact of A-site mixing on defect activity is not fully understood.[3]

The A-site cation indirectly determines various optoelectronic, transport and defect properties via an influence on the symmetry and dynamic response of the crystal lattice. Although defect formation and activity is sensitive to the exact system under consideration, the common observation across OLHPs is that halide ions form abundant, mobile point defects which are active in carrier trapping and recombination.[4,5] Furthermore, the bonding in OLHPs is relatively weak, leading to an easily distorted ('soft') lattice and large lattice relaxation after carrier capture at a defect site.[6,7]

Large lattice relaxation is not commonly observed in all-inorganic photovoltaic materials. It is more akin to what occurs in organic semiconductors,[8] where steric engineering through the incorporation of bulky ligands is used to restrict the vibrational modes associated with lattice relaxation after electronic excitation.[8,9] In this talk I will propose that a similar approach can be used to rationalise the design of defect-tolerant OLHPs. I will present results from first-principles calculations combined with interpolation techniques adapted from the field of molecular materials, and symmetry mode analysis. First I will show that cation mixing in $MA_{1-x}Cs_xPbI_3$ can be used to adjust the non-radiative carrier capture rate at the iodine interstitial by seven orders of magnitude. I will also use this example to demonstrate that defect activity can be tuned by controlling phase formation through the steric size of the molecular cations. This enables defect properties to be tailored through steric engineering, without altering the metal–halide chemistry that is beneficial for photovoltaic performance.

I will discuss and highlight the interplay between halide perovskite composition, structural dynamics and defect physics, and I expect this approach to be transferable to other systems where there is large lattice relaxation – for instance, perovskite analogues or metal-organic frameworks.

References

[1] Q. Jiang, J. Tong, Y. Xian et al., *Nature*, 2022, 10.1038/s41586-022-05268-x

[2] D. R. Ceratti, A. V. Cohen, R. Tenne et al., *Mater. Horiz.*, 2021, **8,** 1570-1586

[3] Jin-Wook Lee, Shaun Tan, Sang Il Seok et al., *Science,* 2022, **375,** 835

[4] M. H. Du, *J. Chem. Phys Lett.,* 2015, **6,** 1461

[5] A. Senocrate and J. Maier, *J. Am. Chem. Soc.,* 2019, **141,** 8382

[6] J. M. Frost and A. Walsh, *Acc. Chem. Res.,* 2015, **49,** 528

[7] L. D. Whalley, P. van Gerwen, J. M. Frost et al., *J. Am. Chem. Soc.,* 2021, **143,** 9123

[8] S. Fratini, M. Nikolka, A. Salleo et al., *Nat. Mater.,* 2020, **19,** 491

[9] R. Crespo-Otero, Q. Li, and L. Blancafort, *Chem. Asian J.,* 2019, **14,** 700-714

$[C(NH_2)_3]Er(HCO_2)_2(C_2O_4)$ – The first hybrid perovskite with negative linear compressibility

Thomas J. Hitchings,[1] Andrew B. Cairns,[2] David Allen[3] and Paul J. Saines.[1]

[1] School of Chemistry and Forensic Science, University of Kent, Canterbury, Kent, CT2 7NH
[2] Department of Materials, Imperial College London, South Kensington Campus,
London, SW7 2AZ,
[3] Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, Oxfordshire

The size of crystalline phases usually has an inverse relationship with increasing hydrostatic pressure as thermodynamically, the overall cell volume must decrease to minimise the increase in Gibbs free energy. Some materials, however, exhibit negative linear compressibility (NLC) along one or two axis at the expense of a larger contraction under pressure in other dimensions. Framework materials consist of metal nodes bridged by organic linkers and form a wide range of topologies with flexible mechanical properties, leading to more than 20 examples exhibiting NLC behaviour.[1,2] Other frameworks with short linkers exist that lack substantial porosity but have large enough voids to incorporate organic cations, generating systems that can adopt analogues of the ABX_3 inorganic perovskites. Such hybrid perovskites have been predicted to exhibit NLC but, to date, no hybrid perovskites have been found to have NLC experimentally.[3,4] A small family of hybrid perovskites, $[A]Er(HCO_2)_2(C_2O_4)$ where $[A]^+ = [C(NH_2)_3]^+$ and $[C(NH_2)_3]^+$ has recently been synthesised and reported, which feature monovalent and divalent organic linkers.[5,6] Variable temperature diffraction experiments found these phases crystalise in the orthorhombic and monoclinic systems and exhibit negative thermal expansion. A recent variable pressure experiment on this family of frameworks found that $[C(NH_2)_3]Er(HCO_2)_2(C_2O_4)$ exhibited NLC behaviour, the first hybrid perovskite material to do so arising from similar hinging of the wine-rack-like framework structure.

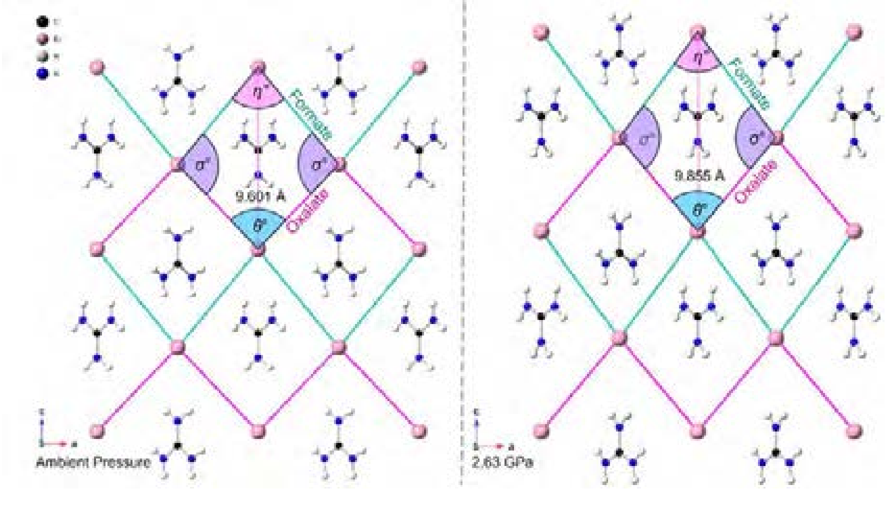


Figure 2. Highlighting the structural changes of $[C(NH_2)_3]Er(HCO_2)_2(C_2O_4)$ under applied hydrostatic pressure.

References

1 Q. Zeng, K. Wang and B. Zou, *Langmuir*, 2022, **38**, 9031–9036.
2 A. B. Cairns and A. L. Goodwin, *Phys. Chem. Chem. Phys.*, 2015, **17**, 20449–20465.
3 Z. Yang, *et al.*, *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, 2019, **377**, 20180227.
4 P. S. Ghosh and I. Ponomareva, *J. Phys. Chem. Lett.*, 2021, **12**, 7560–7565.
5 L. G. Burley, *et al.*, *Dalt. Trans.*, 2021, **50**, 5437–5441.
6 L. G. Burley, *et al.*, *Eur. J. Inorg. Chem.*, 2021, **2021**, 3806–3811.

Imaging Buried Dislocations in Halide Perovskites with 3D Strain Mapping

Kieran W. P. Orr,[1,2] Samuel D. Stranks[1,2]

[1] Department of Physics, Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge, CB3 0HE, UK,
[2] Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge, CB3 0AS, UK,

Halide perovskites have garnered significant attention as materials for use in solar cell and lighting applications, and over the last decade, device efficiencies of halide-perovskite based solar cells have risen from 14.1% (2013)[1] to 25.7% (2022)[2]. However, much of this improvement has been the result of empirical optimisation of fabrication procedures and our understanding of the light absorbing halide perovskite materials lags behind. It has become evident that strain plays an important role in determining device efficiency and long-term stability,[3] but the precise mechanism by which strain affects the materials' optoelectronic properties remains unclear.

In this talk, I will present our recent work investigating the internal structure of the archetypical $MAPbBr_3$ halide perovskite ($MA = CH_3NH_3$) using Bragg coherent diffraction imaging measurements[4] carried out at the Diamond Light Source, UK. This technique allows us to view the atomic displacement fields within our $MAPbBr_3$ material in the form of real space crystal reconstructions (Fig. 1a) which we are able to use to identify ⟨100⟩ and ⟨110⟩ edge dislocations in $MAPbBr_3$ (Fig. 1b). Further, by using *in situ* measurements we also discover that these dislocations become significantly more mobile under illumination with visible light. Solar cells (obviously) must be illuminated during operation, therefore, this light-induced dislocation migration gives us an insight into the buried nanoscale changes occurring in halide perovskite materials during device operation. Further, we intentionally study a subset of crystals that degrade under exposure to the X-ray beam, and by combining the coherent diffraction imaging data with photoluminescence microscopy, we discover that dislocation formation is a key step in material (and therefore device) degradation.

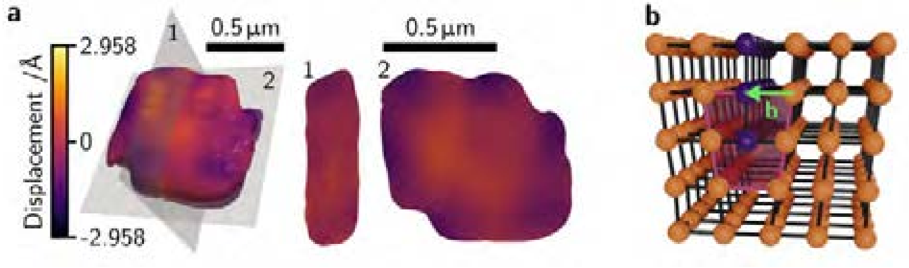


Fig. 1: a Example electron density reconstruction of a $MAPbBr_3$ microcrystal (left), with slices through the 3D volume indicated by the numbered grey planes (middle and right). The colour scale indicates the size of the atomic displacement along the X-ray scattering vector direction. **b** Schematic representation of an edge dislocation. The atoms in purple belong to an extra atomic plane in the top three rows of the structure. The region in pink highlights the highly strained region in the vicinity of the dislocation and the green arrow is the Burgers vector, $\mathbf{b}$.

References

[1] Burschka, J. *et al.*, *Nature*, 2013, **499**, 316–319.
[2] Best Research-Cell Efficiency Chart. https://www.nrel.gov/pv/cell-efficiency.html.
[3] Liu, D. *et al.*, *Nature Materials*, 2021, **20**, 1337–1346.
[4] Miao, J. *et al.*, *Science*, 2015, **348**, 530–535.

21st Century 'White' Gold: Extraction and Recycling

Elizabeth H. Driscoll[1,4], Alex Green[2,4], Erin Budge[1,4], Tianchi Pan[1], Ze He[1], Rob Sommerville[1,4], Rebecca Paisley[3], Ali Salisbury[3], Peter Slater[2,4], and Emma Kendrick[1,4]

[1] School of Metallurgy and Materials, The University of Birmingham, Edgbaston, B15 2SE, UK

[2] School of Chemistry, The University of Birmingham, Edgbaston, B15 2TT, UK

[3] Cornish Lithium Ltd., Tremough Innovation Centre, Penryn, Cornwall, TR10 9TA

[4] The Faraday Institution, Harwell Campus, Didcot OX11 0RA

With the push towards the electrification of infrastructure, to support policy changes and mitigate increasing effects of climate change, there is a necessary drive for electric vehicle (EV) uptake. With the demand for Li-ion battery packs, a simultaneous demand for the critical materials within these packs (cobalt, natural graphite, phosphorus and lithium)[1] is concordant.

The suitability of Li-ion batteries for this application results from this type of battery being a low-weight, high energy density battery, and as the name suggests, lithium plays a critical role in this battery's operation. The majority of global lithium production can be accounted for within 4 countries[2], with lithium resources amounting to 43.6 million tonnes[2], of which 62% are from brines and the rest in mineral form[3]. Within the sourcing of lithium (hard rock, underground reservoirs, and geothermal waters) – the emissions of CO_2, land and water usage needs to be considered too.[4]

Thus, in order to preserve natural resources and avoid another crisis, investigations into lithium recovery from both primary and secondary resources, and working towards a circular economy, is critical. Hence, this body of work will initially highlight how outreach and engagement work has led to a collaboration project with Cornish Lithium Ltd, where work has centred on the recovery of lithium from the geothermal waters. Applying the same principles, secondary resources will also be highlighted, in efforts towards a zero-waste approach waste when considering obtaining the lithium from spent battery materials during the recycling process. To conclude, the talk will focus on the upcycling of electrode materials towards next generation materials, while recovering the lithium.

References

1 European Commission, *Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability*, 2020.

2 U.S Geological Survey, *U.S Geol. Surv.*, 2022, 2021–2022.

3 J. D. Graham, J. A. Rupp and E. Brungard, *Sustainability*, 2021, **13**, 11274.

4 C. Early, The new 'gold rush' for green lithium, https://www.bbc.com/future/article/20201124-how-geothermal-lithium-could-revolutionise-green-energy, (accessed 17 May 2022).

Poster
Abstracts

PyTASER: First-principles transient absorption spectra (TAS) for bulk crystals

Savyasanchi Aggarwal,[1] Alex M. Ganose[2] and Aron Walsh.[3]
[1] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK
[2] Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, UK
[3] Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK.

Transient Absorption Spectroscopy (TAS) is a powerful method to characterise the photophysical response of materials, and has proven indispensable when extracting excited state properties in many molecular systems [1]. However, despite the clear-cut advantages this can provide for solar and energy materials, use of TAS in these systems has been limited by inefficiencies in isolating *pristine* bulk crystals, as well as difficulties in interpreting spectral features in more complex systems, especially upon comparing extrinsic and intrinsic effects.

To combat these problems, we have developed **PyTASER** (https://github.com/WMD-group/PyTASER), a Python-based library and set of command-line tools to simulate TAS spectral features from electronic band structures of pristine bulk materials. Herein, we seek to provide a quick and accurate comparison for experimental spectroscopists to better analyse spectral differences between their materials and the theoretical outputs. Additionally, we hope to provide a concrete link between first-principles calculations and physical observations.

The theoretical basis of PyTASER relies on identifying the Joint Density of States (JDOS) for the "dark" ground state and "light" excited state absorption profiles. JDOS defines the density of allowed vertical transitions between occupied and unoccupied electronic bands within the system, and thus gives an accurate absorption profile for direct bandgap systems. Upon comparing the dark and light JDOS values across an energy mesh, we can compute the difference to find the overall transient absorption profile for the system.

While the use of JDOS is fairly trivial for the 'dark' probe system (as shown in use in similar packages, e.g. AbiPy [2]), the difficulty lies in the modelling of partial occupancies as expected in the "light" system. To account for this, we modelled band electronic occupancies using the Fermi-Dirac distribution, varying the system temperature and the carrier concentration as an analogy to the time-delay between the pump and probe lasers in real-life TAS.

On top of effectively modelling the overall transient absorption profile, the nature of the package allowed extraction of individual band contributions towards the overall spectra. An example is shown in Figure 1, where the overall spectrum is shown in black, while individual band transitions (orange, purple, red) can be clearly assigned to different spectral features.

This feature is not possible to extract in experimental TAS setups without considerable analysis and offers a possibility to drastically accelerate analysis of materials TAS experiments.

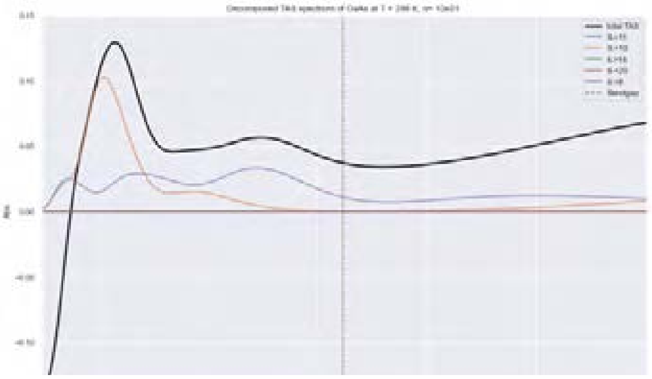


Figure 1: A PyTASER-generated TAS spectrum calculated for GaAs under the conditions of 298 K and a carrier concentration of $n = 10^{21}$ cm^{-3}. The bandstructure data is extracted from the Materials Project Database [3] and the post-processing is done using PyMatGen [4] tools.

1. Kovalenko, S. A., R. Schanz, H. Hennig, and N. P. Ernsting. "Cooling dynamics of an optically excited molecular probe in solution from femtosecond broadband transient absorption spectroscopy." *The Journal of Chemical Physics* **115**, no. 7 (2001): 3256-3273.
2. Gonze, Xavier, François Jollet, F. Abreu Araujo, Donat Adams, Bernard Amadon, Thomas Applencourt, Christophe Audouze et al. "Recent developments in the ABINIT software package." *Computer Physics Communications* **205** (2016): 106-131.
3. Jain, Anubhav, Shyue Ping Ong, Geoffroy Hautier, Wei Chen, William Davidson Richards, Stephen Dacek, Shreyas Cholia et al. "Commentary: The Materials Project: A materials genome approach to accelerating materials innovation." *APL materials* 1, no. 1 (2013): 011002.
4. Ong, Shyue Ping, William Davidson Richards, Anubhav Jain, Geoffroy Hautier, Michael Kocher, Shreyas Cholia, Dan Gunter, Vincent L. Chevrier, Kristin A. Persson, and Gerbrand Ceder. "Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis." *Computational Materials Science* 68 (2013): 314-319

Tuning between ground states in layered perovskite-related materials

Areesha Ali,[1] Emma E. McCabe.[1]

[1] Department of Physics, Durham University, Durham, DH1 3LE

Antiferroelectrics such as $PbZrO_3$ have been a key research focus due to their potential for energy storage devices.[1,2] They adopt an antipolar ground state (with zero polarisation) but under an applied electric field, undergo a phase transition to a low energy, metastable polar (and ferroelectric) phase.[3] Current research aims to find new lead-free antiferroelectric materials.

$Bi_2W_2O_9$ is an *A*-site deficient Aurivillius phase, composed of alternating $(Bi_2O_2)^{2+}$ layers and perovskite-like blocks. It adopts a non-polar ground state (of *Pbcn* symmetry, Figure 1). Our research is motivated by the theory prediction of a metastable polar phase (of $A2_1am$ symmetry) only 34 meV/f.u. above the ground state.[4] This suggests the potential for antiferroelectric behaviour in Aurivillius and related phases.

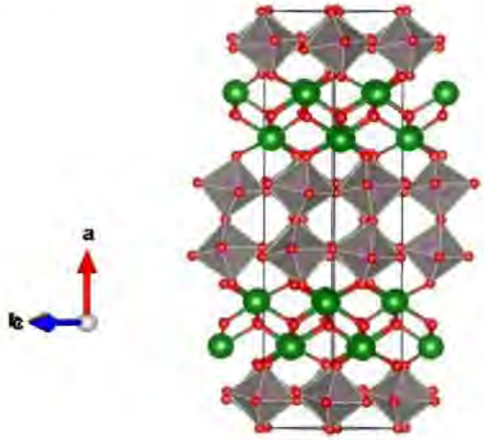


Figure 1: Structure of $Bi_2W_2O_9$ in Pbcn ground state. Bismuth and oxide ions are shown in green and red, and WO_6 octahedra in grey, respectively.

The aim of this project is to understand the mechanisms of ferroelectricity and antiferroelectricity in layered perovskite-related materials. Our experimental work involves tuning the composition to change the relative energies of the polar and antipolar phases and allow us to access the antipolar – polar phase transition.

References

[1] X.-Z. Lu and J. M. Rondinelli, *MRS Advances*, 2020, **5**, 3521-3545.

[2] C. A. Randall, Z. Fan, I. Reaney, L. Q. Chen and S. Trolier-McKinstry, *J. Am. Ceram. Soc.*, 2021, **104**, 3775-3810.

[3] Tolédano, P.; Guennou, M., Theory of antiferroelectric phase transitions. *Physical Review B* 2016, ***94* (1)**, 014107.

[4] H. Djani, E. E. McCabe, W. Zhang, P. Halasyamani, A. Feteira, J. Bieder, E. Bousquet and P. Ghosez, *Phys. Rev. B*, 2020, **101**, 134113.

Increase In Critical Current Density Achieved in Li-Stuffed Garnet by Integrated Perovskite Secondary Phase

Sebastian J. Altus[1*], Innes McClelland[1], Denis Cumming[2], Edmund J. Cussen[1]

[1]Dept. of Materials Science and Engineering, The University of Sheffield

[2]Dept. of Chemical and Biological Engineering, The University of Sheffield

*Presenting Author: sjaltus1@sheffield.ac.uk

Solid-state batteries have become a promising alternative to the conventional Li-ion battery as an energy source. However, challenges of Li dendritic growth are still much of a hinderance to the large scale adoption of this technology.[1] Forming at critical current densities far below current commercialisation targets Li metal dendrites are proving to be an obstacle to the wide scale implementation of the technology.[2,3] One source of formation and propagation of Li dendrites has been identified by researchers as high electronic conductivity in solid electrolytes.[4]

We have elected to introduce transition metals into the $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ garnet systems to induce a change in electronic conduction. Changing the electronic conduction through the solid electrolyte allowed for controlled investigation into electrochemical properties and Li dendrite formation behaviour. Powder X-ray diffraction (PXRD) analysis was performed on Garnet $Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$ (x = 0.035, 0.05, 0.07, 0.105) following synthesis, here the formation of a composite structure was observed, the target cubic phase $Ia\overline{3}d$ was synthesised along with the presence of a perovskite-related *n* = 1 Ruddlesden-Popper secondary phase La_3LiMnO_7. PXRD analysis following pelleting via plasma spark sintering found the predominant garnet phase to have been retained whilst the secondary phase was observed to undergo a phase transformation to *n* = 2 La_4LiMnO_8. Initial AC impedance and DC polarisation, undertaken to investigate the effect of the secondary phase on the electrochemical properties of the compound, revealed minor changes in electronic and ionic conductivity up x = 0.07. To further understand the role of Li metal in contact, and during cycling with the solid electrolyte, AC impedance and galvanostatic cycling were performed. Results revealed increasing amounts secondary phase reduced resistance in contact with Li, subsequently leading to an increase in critical current density (CCD). A natural solubility limit however appears to be reached at x = 0.07, whereupon the secondary phase counteracts the interfacial resistance, thereby reducing the CCD. This work provides an intriguing insight into the role of secondary phases within solid electrolytes, with different electrochemical properties they appear, even at low levels, to affect the electrochemical attributes of the whole system.

References

1 K. B. Hatzell, X. C. Chen, C. L. Cobb, N. P. Dasgupta, M. B. Dixit, L. E. Marbella, M. T. McDowell, P. P. Mukherjee, A. Verma, V. Viswanathan, A. S. Westover and W. G. Zeier, *ACS Energy Lett.*, 2020, **5**, 922–934.

2 J. Kasemchainan, S. Zekoll, D. Spencer Jolly, Z. Ning, G. O. Hartley, J. Marrow and P. G. Bruce, *Nat. Mater. 2019 1810*, 2019, **18**, 1105–1111.

3 F. Flatscher, M. Philipp, S. Ganschow, H. M. R. Wilkening and D. Rettenwander, *J. Mater. Chem. A*, 2020, **8**, 15782–15788.

4 F. Han, A. S. Westover, J. Yue, X. Fan, F. Wang, M. Chi, D. N. Leonard, N. J. Dudney, H. Wang and C. Wang, *Nat. Energy*, 2019, **4**, 187–196.

Nanocrystalline Cerium Germanates For Use As Oxygen Storage Materials

James W. Annis,[1] Janet M. Fisher,[2] David Thompsett[2] and Richard I. Walton.[1]

[1] University of Warwick, Coventry, West Midlands, CV4 7AL

[2] Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH

CeO_2/ZrO_2 solid solutions are the most commonly used oxygen storage materials for catalytic converters.[1] This is due to a number of factors, including the relative ease of the conversion between the CeO_2 and Ce_2O_3 redox pair; the thermal stability of the material; and the high lattice oxide mobility of the structure.

Due to the need to meet the ever-increasing demands of vehicle emission regulations, new materials are being studied to see if they can outperform the current industry standards. Our work has involved the hydrothermal synthesis of $CeGeO_4$, a scheelite structured material[2] that is capable of reduction to $Ce_2Ge_2O_7$ and then reoxidation under mild conditions. These materials have been studied using X-ray and neutron diffraction experiments, with Rietveld analysis of average structure, TEM and EDX imaging, and reduction experiments such as TPR (temperature programmed reduction).

Three different cerium germanates have been observed and characterised. We have also developed solid solutions of $CeGeO_4$ with another scheelite material[3], $CaWO_4$, to see if that can improve the oxygen storage properties.

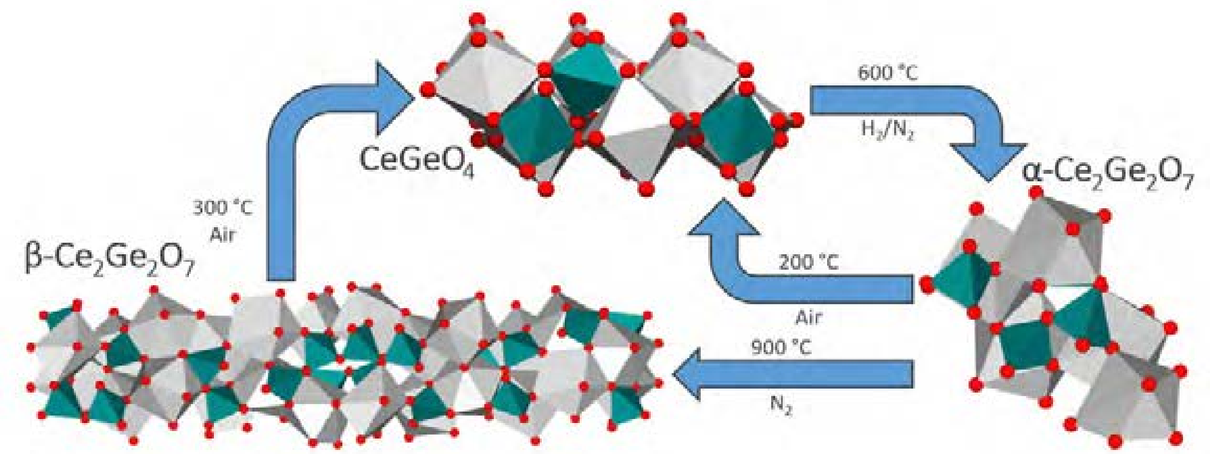


Figure 3 - The unit cells of three cerium germanate materials and the heat and atmospheric conditions needed to convert between them.

References

1 J. Kašpar, P. Fornasiero and N. Hickey, *Catal Today*, 2003, **77**, 419–449.

2 J. Li, C. Zhao, F. Lan, F. Chen, C. Teng, Q. Yan and J. Tang, *Catal Commun*, 2016, **77**, 26–31.

3 M. I. Kay, B. C. Frazer and I. Almodovar, *J Chem Phys*, 1964, **40**, 504–506.

Ion Transport and Interfacial Dynamics in Thioborate Solid Electrolytes

Alexander J. H. Bell,[1,2] Karen E. Johnston[2] and James A. Dawson.[1]

[1] School of Natural and Environmental Sciences, Newcastle University, UK

[2] Department of Chemistry, Durham University, UK

All-solid-state batteries are a promising route toward delivering improvements to both the performance and safety characteristics necessary for next-generation battery cells. One class of potential solid electrolyte materials are lithium thioborates, such as Li_3BS_3 and $Li_6B_7S_{13}X$ (X = Cl, Br, I), owing to their high conductivities in concert with favourable decomposition products, widening the electrochemical window across high-performance interphases. We present some of the current challenges facing solid electrolyte incorporation into battery cells and this favourable-decomposition approach, with our current and future research toward optimising thioborate properties.

Crystal growth of $A_3Bi_2X_9$ ($A = CH_3NH_3^+$, $NH_2HCNH_2^+$, Cs^+, Rb^+ and $X = Cl^-$, Br^-, I^-) in Silica Gel

P. Bhatt,[1,*] A. Regoutz,[1] and R. G. Palgrave[1]
[1]*Department of Chemistry, University College London,*
20 Gordon Street, London, WC1H 0AJ, United Kingdom

(Dated: June 18, 2022)

Lead-free halide perovskites (ABX_3) and perovskite-related structures, such as the vacancy ordered perovskites (A_2BX_6, $A_3B_2X_9$) are well-established for their application potential in solar cells due to their enhanced optical and electrical properties.[1] Beyond solar cells, applications are also include LEDs, X-ray detectors in healthcare and gas sensing.[2][3]

Single crystals of perovskite materials prove to be advantageous as they are able to circumvent issues of unwanted defect inclusion in materials, provide a large active area, longer carrier diffusion lengths and higher attenuation.[4][5][6] Current single crystal growth mechanisms either require specialised apparatus (Bridgman growth) or are solution based - where crystals nucleate in the liquid medium. Liquid medium growth modes show difficulties, mainly the formation of defects as a result of convection currents - causing imperfections such as point defects and lattice strains.[7]

We present a cost effective method of crystal growth for halide perovskites in gel based systems. Conducting crystal growth in gels separates itself from such methods as formation of crystals occurs in a colloidal, semi-solid medium. A gel is described as a system with two phases (solid and liquid) wherein, the solid phases forms a loosely linked polymer[8] that the liquid phase is able to permeate.[9] Commonly used gels for crystal growth include agar, bentonite, gelatin, polyacrylamide and silica. Of these, this work presents crystal growth with silica gels, which has been the most extensively studied.

The formation of crystals in gels is heterogeneous, but unlike pure solution and liquid based systems, the growth mechanism is dominated by diffusion rather than convection. Crystal growth in gels is described as nucleation by diffusion.[7] As such, *Fick's law* is able to formalise the gel growth mechanism.[9] Figure 1 (a), (b) illustrates two growth modes, single and dual diffusion. Using the silica gel medium, vacancy ordered perovskites $A_3Bi_2X_9$ ($A = CH_3NH_3^+$, $NH_2HCNH_2^+$, Cs^+, Rb^+ and $X = Cl^-$, Br^-, I^-) (Figure 1 (c)) are synthesised and characterised using X-ray Diffraction, X-ray Photoelectron Spectroscopy and Raman Spectroscopy. Additionally, diffusion coefficients for the precursors of the synthesised crystals are found and calculated using UV-visible spectroscopy and Fick's Law. With the successful formation of single crystals, future work will include doping at the B- and X-site using the silica medium and calculating X-ray detection limits, electron transport and ion mobility analysis to assess feasibility for high performance X-ray detection and light absorption in solar cells.

FIG. 1. Schematic of (a) single diffusion and (b) dual diffusion growth systems (c) $(CH_3NH_3)_3Bi_2I_9$ grown by single diffusion

---

[1] L. Chouhan, S. Ghimire, C. Subrahmanyam, T. Miyasaka, and V. Biju. *Chem. Soc. Rev.*, 49(10):2869–2885, 2020.
[2] H. Kim, J. Han, J. Choi, S. Kim, and H. Jang. *Small Methods*, 2(3):1700310, 2018.
[3] X. Li, P. Zhang, Y. Hua, F. Cui, X. Sun, L. Liu, Y. Bi, Z. Yue, G. Zhang, and X. Tao. *ACS App. Mat. & Inter.*, 14(7):9340–9351, 2022.
[4] L. Chen, Y. Tan, Z. Chen, T. Wang, S. Hu, Z. Nan, L. Xie, Y. Hui, J. Huang, Chao Zhan, et al. *ACS*, 141(4):1665–1671, 2019.
[5] H. Zhang, Y. Xu, Q. Sun, J. Dong, Y. Lu, B. Zhang, and

[*] prajna.bhatt.17@ucl.ac.uk

A potential thermoelectric material: zinc-based oxysulfide $SrZn_2S_2O$

Shipeng Bi[a,b], Katarina Brlec[a,b], David O. Scanlon[a,b]

[a] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

[b] Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, United Kingdom

In the process of primary energy consumption, a large amount of waste heat is generated. Thermoelectric materials can convert waste heat energy into electric energy, which is crucial to solving the current energy crisis and global warming. In general, the performance of thermoelectric materials can be determined by the dimensionless figure of merit, ZT, that evaluates electronic and thermal properties. However, it is difficult to maximize ZT due to the interaction between different parameters. Although some high ZT thermoelectric materials such as bismuth chalcogenide and lead telluride have been found, they have not been widely used because they contain rare or toxic elements.

Recently, $SrZn_2S_2O$ was proposed as a novel photocatalyst for water splitting applications.[1] Because of its relatively high melting point, combined with the low toxicity and easy synthesis property of oxides, we think that $SrZn_2S_2O$ may be a potential thermoelectric material. Using density functional theory (DFT), we first studied the phononic stability of $SrZn_2S_2O$. Then based on the $SrZn_2S_2O$ electronic structure calculated with hybrid-DFT, electronic transport properties were calculated using AMSET[2]. Our ultimate goal is to calculate ZT and characterize $SrZn_2S_2O$ as a thermoelectric material.

References

[1] S. Nishioka, T. Kanazawa, K. Shibata, Y. Tsujimoto, H.-C. Loye, and K. Maeda, *Dalton T.*, 2019, **48**, 15778–15781.

[2] A. M. Ganose, A. J. Jackson, D. O. Scanlon, *Nat. Commun.*, 2021, **12**, 2222.

Probing Li-ion Conductivity in a Material with a $Sc_2(WO_4)_3$ Framework

Colm W. Boyle,[1] Fraser Barclay[1], Nathan Cox[1], Constance Aucler[1], Matthew Friskey[1],
Thomas Proffen[2], Julia L. Payne[1]

[1] School of Chemistry, University of St Andrews, St Andrews, Scotland. KY16 9ST

[2] Spallation Neutron Source, Oak Ridge National Laboratory, 1 Bethel Valley Road
Oak Ridge, TN 37830

In recent years polyanionic materials have been explored for use as Li-ion battery electrodes due to their tunability and large electrochemical stability window. The area of sulfate-based Li-ion solid state electrolytes (SSEs) has not received attention despite other types of oxides and polyanionic materials being studied heavily: $Li_{3x}La_{(2/3)-x}\square_{(1/3)-2x}TiO_3$, $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, $Li_{14}ZnGe_4O_{16}$.[1] Advantages of sulfate-based Li-ion SSEs are the degree of tunability, stability and ease of synthesis.

$Li_2Mg_2S_3O_{12}$ was first reported by Touboul *et al.* and it consists of a $Sc_2(WO_4)_3$-type framework. The $Sc_2(WO_4)_3$ structure type is closely related to the NASICON structure but differs in the stacking of octahedral and tetrahedral units. The $Sc_2(WO_4)_3$-type similarly contains cavities which hold Li-ions.[2] In this work, we investigate increasing the phosphorus content in $Li_{2+x}Mg_2S_{3-x}P_xO_{12}$ to increase the Li-ion content. We have used several techniques to characterise $Li_{2+x}Mg_2S_{3-x}P_xO_{12}$ including powder X-ray diffraction (PXRD), powder neutron diffraction (PND), electron microscopy and electrochemical impedance spectroscopy. As P^{5+} and S^{6+} are isoelectronic, it is not possible to probe P/S substitution using PXRD, so PND was used. Combined refinements using PXRD and PND data have been used to identify new Li-sites and to calculate how Li-Li distances change upon P-doping. Using the software softBV, we calculate the bond valence energy landscapes to probe the Li-migration pathways in our samples ($Li_{2+x}Mg_2S_{3-x}P_xO_{12}$ (x = 0-0.3)).[3] Electrochemical impedance spectroscopy shows an increase in lithium-ion conductivity of 2 orders of magnitude for the doped material (2.4×10^{-3} S cm^{-1} at 400 °C).

References

[1] P Knauth, *Solid State Ionics*, 2009, **108**, 911-916.

[2] M.Touboul, E.Le Samedi, M.Quarton, *J. Less Common Metals*, 1989, **146**, 67-73.

[3] L. L. Wong, K. C. Phuah, R. Dai, H. Chen, W. S.Chew, and S. Adams, *Chem. Mater.*, 2021, **33**, 625−641.

Tuning ternary (oxide) nitrides through disorder and composition

Joachim Breternitz[1] and Susan Schorr.[1,2]

[1] Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, 14109 Berlin,

[2] Freie Universität Berlin, Malteserstr. 74-100, 12249 Berlin.

Although solar cells are widely commercialised, the current dominant technology based on crystalline silicon suffers from the indirect bandgap of silicon. This dictates that such modules are comparably heavy, thick and inflexible. Substitutes, such as CdTe, $Cu(Ga,In)S_2$ or lead halide perovskites, on the other hand, contain very scarce elements – such as Te & In – or very toxic elements – such as Cd & Pb, which would prevent their large-scale use. Therefore, finding alternative semiconductor materials with suitable properties and their thorough characterisation remains a task of uttermost importance for the widespread use of renewable energies.

One of those alternatives are ternary nitride materials in wurtzite-derived crystal structures. In a way, they can be rationalised as (In,Ga)N derived compounds, in which the trivalent cations are replaced through heterovalent substitutions with divalent and tetravalent cations. We have focussed our attention to the exemplary system $ZnGeN_2$, which we access through ammonolysis reaction of Zn_2GeO_4 precursor materials[1] and for which we uncovered the chemical reaction mechanism, facilitating the targeted synthesis of oxide nitride materials with a defined composition.[2]

The increased structural and chemical complexity of such ternary nitrides, expresses in the crystallisation of $ZnGeN_2$ in the orthorhombic ß-$NaFeO_2$-type, a low symmetry subgroup of the wurtzite-type crystal structure.[3] This does, however, also open the pathway for a bandgap tuning mechanism through disorder of the cations over the two crystallographic cation sites,[4] which is unique for such ternary compounds. Using a combination of in-depth chemical knowledge, X-ray and neutron powder diffraction, we can show that this intrinsic disorder mechanism exists and is independent of the oxygen content of the material, although oxygen also influences the bandgap of the material in a similar manner.[5]

References

[1] J. Breternitz, Z. Wang, A. Glibo, A. Franz, M. Tovar, S. Berendts, M. Lerch, S. Schorr, *Phys. Status Solidi A,* 2019, **216**, 1800885.

[2] Z. Wang, D. Fritsch, S. Berendts, M. Lerch, J. Breternitz, S. Schorr, *Chem. Sci.,* 2021, **12**, 8493–8500.

[3] J. Breternitz, S. Schorr, *Acta Cryst A,* 2021, **77**, 208–216.

[4] P. C. Quayle, E. W. Blanton, A. Punya, G. T. Junno, K. He, L. Han, H. Zhao, J. Shan, W. R. L. Lambrecht, K. Kash, *Phys. Rev. B,* 2015, **91**, 205207.

[5] J. Breternitz, S. Schorr, *Faraday Discuss.,* 2022, **239**, 219–234.

A promising novel n-type thermoelectric $Y_2Ti_2O_5S_2$

Katarina Brlec[1,2] and David O. Scanlon.[1,2]

[1] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK

[2] Thomas Young Centre, University College London, Gower Street, London, WC1E 6BT, UK

One of the many pathways to decreasing the impact of climate change is to increase the efficiency of current fossil fuel based systems. Even the best internal combustion engines suffer from thermal losses where up to 70% of energy is lost as exhaust heat. These losses can be offset to an extent by thermoelectric devices which convert waste heat into useful electrical energy via the Seebeck effect. The efficiency of thermoelectric materials is typically evaluated using the figure of merit (ZT), with some of the best performing materials reaching ZTs greater than 2.[1] However, current state-of-the-art thermoelectric materials often contain rare or toxic materials, making them commercially unappealing.

$Y_2Ti_2O_5S_2$ has been experimentally and computationally studied as a potential battery anode and photocatalyst for water-splitting.[2-4] Our recent work shows the intrinsically n-type $Y_2Ti_2O_5S_2$ is also a promising high temperature thermoelectric, with ZT exceeding 1 above 850 K at charge carrier concentrations of 10^{19}–10^{20} cm^{-3}.[5] Using hybrid density functional theory we investigate the intrinsic defect chemistry to determine the doping potential. Select n-type extrinsic dopants were considered to establish whether the charge carrier concentrations required for high ZT are indeed achievable.

References

[1] L. D. Zhao, S. H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid and M. G. Kanatzidis, *Nature*, 2014, **508**, 373–377.

[2] K. McColl and F. Corà, *J. Mater. Chem. A*, 2021, **9**, 7068–7084.

[3] G. Hyett, O. J. Rutt, Z. A. Gál, S. G. Denis, M. A. Hayward and S. J. Clarke, *J. Am. Chem. Soc.*, 2004, **126**, 1980–1991.

[4] Q. Wang, M. Nakabayshi, T. Hisatomi et al., *Nat. Mater.*, 2019, **18**, 827-832.

[5] K. Brlec, K. B. Spooner, J. M. Skelton, D. O. Scanlon, *J. Mater. Chem. A.,* 2022, **10**, 16812-16824

Solid-state chemistry for quantum materials with strong spin-orbit coupling

Alexander J. Browne[1] and Alexandra S. Gibbs.[1,2,3]

[1] School of Chemistry, University of St Andrews, St Andrews, UK,

[2] ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Harwell Campus, UK,

[3] Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany.

Spin-orbit coupling is a quantum effect that gives rise to exotic electronic and magnetic states in the compounds of the 4d and 5d transition metals. However, these exotic states have an extremely sensitive dependence on the structure, composition and bonding – the *chemistry* – of the host materials (Figure 1). Great care in their synthesis and characterisation is therefore required if structure-property relationships are to be correctly determined. With many topical quantum materials also being of interest in electrochemical and catalysis research, the contributions of solid-state chemists to developing understanding and making cross-disciplinary connections is vital.[1]

I will illustrate this challenge through our attempts to unravel the 'true' behaviour of the hexagonal perovskites $BaIrO_3$ and $Ba_4Ir_3O_{10}$. The physical properties reported in previous studies of each these materials are wildly inconsistent – for example, $Ba_4Ir_3O_{10}$ has recently been suggested to have an antiferromagnetic or a quantum spin-liquid ground state, despite the measured crystals being structurally-similar in each case.[2,3] Through an exploration of different synthesis methods, chemical and physical characterisation, and high-resolution neutron diffraction, we are identifying the subtle perturbations in the chemistry of these enigmatic materials that explains the extreme sensitivity of their properties.

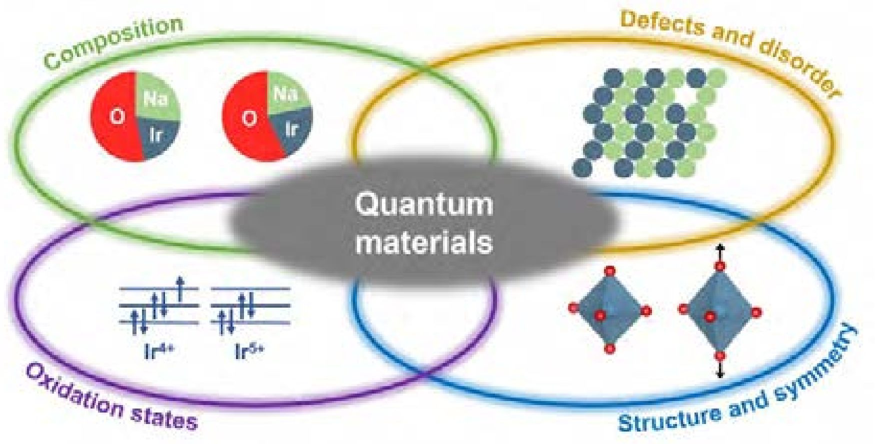


Figure 1: Solid-state chemistry is essential for the understanding of quantum materials

References

[1] A. J. Browne, A. Krajewska and A. S. Gibbs, *J. Mater. Chem. C*, 2021, **9**, 11640.
[2] G. Cao et al., *npj Quant. Mater.*, 2020, **5**, 26.
[3] X. Chen et al., *Phys. Rev. B*, 2021, **103**, 224420.

Thermodynamic signatures of broken chains in dilute quasi-one-dimensional magnets: theory and experiment.

Johnathan Bulled[1], Mario Falseperna[2], Paul Saines[2], Andrew Goodwin[1]
[1]Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR,
[2]School of Physical Sciences, University of Kent, Canterbury, CT2 7NH

One-dimensional motifs are common in the solid state, from magnetic[1] and ferroelectric order[2] to charge density waves (CDWs).[3] Such systems exhibit unique behaviour resulting from low-dimensionality and weak interactions between motifs. A useful signature for the characterisation and parameterisation of quasi-one-dimensional (q-1D) materials is found in their heat capacity: a broad peak at higher temperature associated with order along the chain, is separated from a sharp, low temperature feature associated with final three-dimensional order.[2] However, many quasi-one-dimensional systems contain defects, either intentionally or accidentally; we show here that the heat-capacity signature of q-1D systems is very sensitive to the inclusion of small concentrations of nonmagnetic defects (dilution). This sensitivity is due to the unique property of 1D motifs: even a small number of defects segments the chains. A combination of Monte Carlo and mean field theory are used to identify several thermodynamic signatures of this chain breaking.

Turning to the experimental solid solution $\mathrm{Tb}_{1-x}\mathrm{Y}_x(\mathrm{HCOO})_3$, the $x = 0$, 0.05, 0.1, 0.2 and 0.4 members of the series were synthesised, characterised and heat capacity was measured down to $T = 0.3$ K. The Hamiltonian of the $x = 0$ member shows in-chain interactions a two orders of magnitude stronger than interchain interactions[4] and is applied here to Monte Carlo simulations across the series. The results, shown in Figure 1, compare well between experiment and theory, which suggests that even at the lowest experimental temperature, disorder is expected due to chain segmentation. Although studied here in a magnetic context, these findings have potential applications in studying q-1D ferroelectrics, CDWs, and to tuning caloric effects.

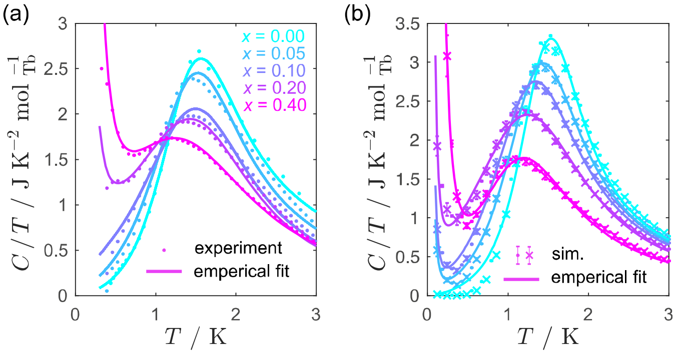


Figure 1: A comparison of (a) experimental heat capacity to (b) the results of a Monte Carlo simulation for the solid solution $\mathrm{Tb}_{1-x}\mathrm{Y}_x(\mathrm{HCOO})_3$ (the value of x is indicated by colour), comparing both to an empirical fit. The gradual suppression of the high temperature feature and growth of a feature at low temperature with increasing x are presented as signatures of chain segmentation.

References

[1] C. P. Landee, R. Kuentzler and J. J. M. Williams, *J. App. Phys.*, 1990, 67, 5604.
[2] K. Kumari and S. Y. Park, *Phys. Rev. B*, 2022, 106, 12
[3] J. W. Lynn, M. Iizumi, G. Shirane, S. A. Werner, and R. B. Saillant, *Phys. Rev. B,* 1975, **12**, 1154.
[4] D. R. Harcombe, P. G. Welch, P. Manuel, P. J. Saines, and A. L. Goodwin, *Phys. Rev. B*, 2016, **94**, 174429.

Fluorine-Rich Oxyfluoride Spinel $Li_{1.25}Ni_{0.625}Mn_{1.125}O_3F$ Utilizing Redox-Active Ni and Mn for High Capacity and Improved Cyclability

Hong Cai,[1] Ruiyong Chen,[1] Mounib Bahri,[2] Cara J. Hawkins,[1] Manel Sonni,[1] Luke M. Daniels,[1] Jungwoo Lim,[1,3] Jae Evans,[1] Marco Zanella,[1] Leanne A. H. Jones,[3,] Troy D. Manning,[1] Tim D. Veal,[3] Laurence J. Hardwick,[1,3] Matthew S. Dyer,[1] Nigel D. Browning,[2] John B. Claridge,[1] Matthew J. Rosseinsky[1]

[1] Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD, Liverpool
[2] Albert Crewe Centre, University of Liverpool, Research Technology Building, Elisabeth Street, Pembroke Place, L69 3GE, Liverpool,
[3] Stephenson Institute for Renewable Energy, University of Liverpool, Peach Street, L69 7ZF, Liverpool

The battery market has grown tremendously over the past decades and continues to expand rapidly. The rapid growth of the lithium-based energy storage market requires high capacity and high voltage cathode materials.[1, 2] Promising cathode materials must be able to accept and release lithium ions reversibly and quickly. Compared to traditional cathode materials, improvements are needed to extend the accessible capacity and cyclability during the development of advanced cathode materials for lithium ion batteries.

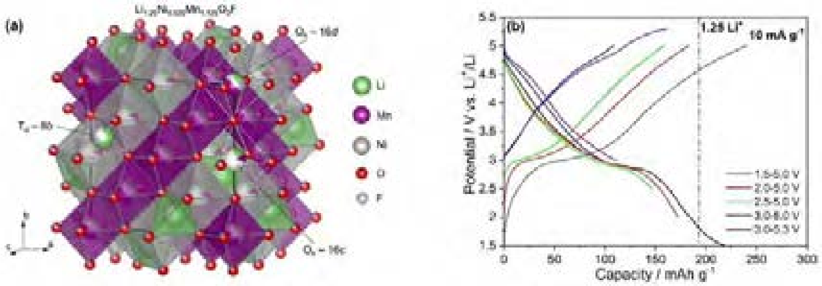


Figure 1: a) Structure of $Li_{1.25}Ni_{0.625}Mn_{1.125}O_3F$ spinel with different sites labelled by type b) Galvanostatic charge/discharge profiles for 8th cycles of the cells tested with different cut-off potential ranges at a current density of 10 mA g^{-1}

By taking the advantage of structural similarity of two spinel compounds $LiNi_{0.5}Mn_{1.5}O_4$ and Li_2NiF_4, a new oxyfluoride spinel $Li_{1.25}Ni_{0.625}Mn_{1.125}O_3F$ ($Fd\bar{3}m$) was successfully synthesised. This spinel crystal structure with significant cation disorder (Figure 1a) was solved by combined refinement of X-ray and neutron diffraction data, and further characterised by electron microscopy and elemental analysis. $Li_{1.25}Ni_{0.625}Mn_{1.125}O_3F$ utilizes redox reactions of both Ni and Mn, accessing capacities of 225 (*i.e.,* 1.46 Li^+ capacity) and 285 mAh g^{-1} (*i.e.,* 1.85 Li^+ capacity) at 25 °C and 40 °C, respectively, through intercalation of additional Li^+ into the lattice. Figure 1b shows the charge/discharge profiles at 8th cycles measured at 10 mA g^{-1} and various cut-off potential ranges (25°C).

Ex situ compositional, structural and spectroscopic analysis of samples at different states of charge/discharge confirm a single-phase intercalation reaction and high structural integrity over cycling. Compared to lithium transition metal disordered rocksalt[3, 4] or spinel-like oxyfluorides[5] previously reported, $Li_{1.25}Ni_{0.625}Mn_{1.125}O_3F$ shows significantly improved cycling stability. The increased fluorine content enables further incorporation of the formally lower charged Ni^{2+}, reflecting the opportunities to control site occupancies and oxidation states via the charge on the anion sublattice new oxyfluoride cathodes.

References

[1] A. Manthiram, *Nat. Mater*, 2020, **11**, 1550.
[2] J. L. Shi. et al, *Adv. Mater*. 2018, **30**, 1705575
[3] R. Chen. et al, *Adv. Energy Mater*, 2015, **5**, 1401814.
[4] R. A. House. et al, *Energy Environ. Sci*, 2020, **11**, 1550.
[5] H. Ji. et al, *Nat. Energy*, 2020, **5**, 213-221.

Cation-disordered $LiNiO_2$ as a cathode for Li-ion batteries

Javier Castells-Gil,[1] Bo Dong,[1] Farheen N. Sayed,[2] Cheng Li,[3] Clare P. Grey,[2] Peter R. Slater,[1]
Phoebe K. Allan,[1]

[1] School of Chemistry, Haworth Building, University of Birmingham, Edgbaston, B15 2TT, Birmingham, U.K.
[2] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

[3] Neutron Scattering Division, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN, 37830 USA

Lithium-rich cation-disordered rocksalt (DRS) oxides are attracting a great deal of attention as the next generation high energy Li-ion cathode materials given their exceptionally high capacities (~ 300 mA h g^{-1}), and their high chemical versatility that allows for a variety of metal compositions whilst facilitating the solubility of doping species for enhanced stability and electrochemical properties.[1][2] Unlike common layered transition metal oxide cathodes, such as $Li(Ni,Mn,Co)O_2$, this family of disordered oxides consist of a cubic NaCl structure in which the Li and transition metal ions are disordered throughout the structure as in a solid solution. This can lead to different degrees of short-range order depending on the composition, which can in turn have an effect on the electrochemical performance.[3] Moreover, the disordered arrangement of cations in the DRS cathodes allows for smaller, isotropic volume changes than those observed in the layered cathodes upon consecutive lithiation/de-lithiation processes, which can help mitigate the long-term stability issues of cathodes due to the particle cracking resulting from the large volume changes.

In this work, we report the mechanochemical synthesis and electrochemical properties of the cation disordered $LiNiO_2$ with an unprecedented 1:1 Li:Ni ratio. We show how the introduction of disorder in $LiNiO_2$ slightly reduces the average working voltage but has, in turn, a positive effect on the cycling stability at high current densities without reducing the overall capacity of the material. Moreover, we make use of local characterisation techniques like Pair Distribution Function (PDF) analysis of X-ray and neutron total scattering measurements and solid-state NMR to study the local structure of Li-ions within the cation disordered network to correlate the presence of short-range ordering in the material with its electrochemical properties.

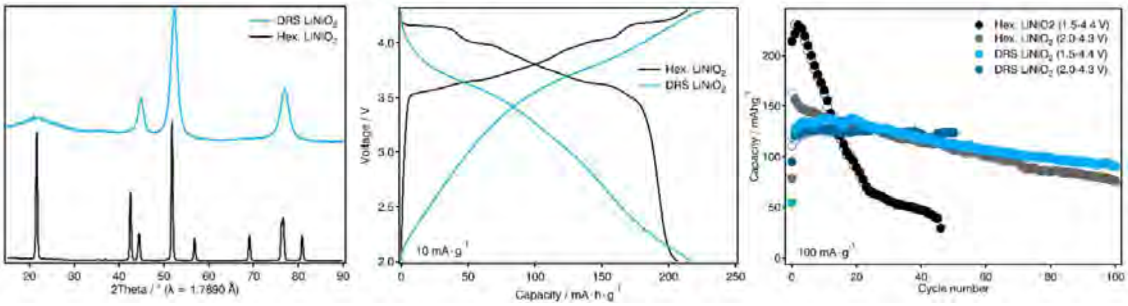


Figure 1 – Powder X-ray diffractograms (*left*); electrochemical capacity *versus* voltage curves (*middle*), and cycling stability in different voltage windows (*right*) of pristine LNO before and after the transformation to a disordered rock salt.

References

[1] R. J. Clément, Z. Lun, G. Ceder, Cation-disordered rocksalt transition metal oxides and oxyfluorides for high energy lithium-ion cathodes, Energy Environ. Sci. 2020; 13:345.

[2] W. D. Richards, S. T. Dacek, D. A. Kitchaev, G. Ceder, Fluorination of Lithium-Excess Transition Metal Oxide Cathode Materials, Hidden structural and chemical order controls lithium transport in cation-disordered oxides for rechargeable batteries, Adv. Energy Mater. 2018; 8:1701533.

[3] H. Ji, A. Urban, D. A. Kitchaev, D. H. Kwon, N. Artrith, C. Ophus, W. Huang, Z. Cai, T. Shi, J. C. Kim, H. Kim, G. Ceder, Nat. Commun. 2019; 10:592.

Exploring compounds in the Li-Ni-O space through ab initio random structure searching

Jiayi Cen,[1,2,3] Bonan Zhu[1,2,3] and David O. Scanlon[1,2,3]

[1]Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom,

[2]The Faraday Institution, Quad One, Harwell Science and Innovation Campus, Didcot OX11 0RA, United Kingdom,

[3]Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, United Kingdom.

The Li-Ni-O phase diagram contains several electrochemically active ternary phases. Most compositions and structures of those ternary phases have very specific growth environments, meaning that they can easily be altered by (electro-)chemical processes, yielding many more (meta-)stable structures with interesting properties.[1,2] In this study, we use ab initio random structure searching (AIRSS) to explore the chemical space containing Li, Ni and O to accelerate materials discovery.[3] We find that AIRSS can efficiently explore structures (e.g. $LiNiO_2$) displaying dynamic Jahn-Teller effects. A thermodynamically stable $Li_2Ni_2O_3$ phase which reduces the thermodynamic stability window of $LiNiO_2$ was discovered. AIRSS also encountered many other dynamically stable structures. Therefore, we confirm the presence of metastable Li-Ni-O phases by revealing their structures and properties. This would allow Li-Ni-O phases to be more easily identified in future experiments and help to combat the challenges in synthesizing Li-Ni-O phases.

References

[1] M. Bianchini, A. Schiele, S. Schweidler, S. Sicolo, F. Fauth, E. Suard, S. Indris, A. Mazilkin, P. Nagel, S. Schuppler, M. Merz, P. Hartmann, T. Brezesinski and J. Janek, *Chem. Mater.*, 2020, **32**, 9211–9227.

[2] M. Bianchini, M. Roca-Ayats, P. Hartmann, T. Brezesinski and J. Janek, *Angew. Chem. Int. Ed.*, 2019, **58**, 10434–10458.

[3] C. J. Pickard and R. J. Needs, *J. Phys.Condens. Matter*, 2011, **23**, 053201.

Preliminary Investigations into Anode Materials for All Solid-State Potassium-ion Batteries

Xin Chen,[1] Fabian Jeschull[2] and Julia Payne[1].

[1] School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, UK, KY16 9ST

[2] IAM, Karlsruhe Institute of Technology, Karlsruhe, Germany, 76131

Potassium-ion batteries (KIBs) are receiving increasing attention as a complementary and alternative technology to lithium-ion batteries. As potassium ions insert/deinsert into electrodes during battery cycling, they cause excessive volume expansion, damaging the electrodes, which greatly reduces the lifetime of the batteries. Many liquid electrolytes are flammable, which makes it desirable to replace them with solid state electrolytes. Polymer electrolytes are less brittle than inorganic solid state electrolytes and can accommodate changes in volume of electrode materials upon cycling. However, there is a need for negative electrode materials which are compatible with polymer electrolytes, which in turn will improve the performance and safety of potassium ion batteries.

In previous work carried out at KIT, a polymer solid electrolyte with PEO and KTFSI was been developed and tested in a potassium metal half-cell by using a Prussian Blue positive electrode.[1] Due to the danger of using potassium metal, safer negative electrodes are required to replace the reference electrode, potassium metal, in KIB studies. Titanium-based materials are one of the most studied anodes for KIBs. As reported in recent studies, $K_2Ti_4O_9$ can reach a discharge capacity of 80 mAh g^{-1} at a rate of 0.8C with liquid KPF_6-based electrolyte.[2] Materials like $Li_4Ti_5O_{12}$ and $Na_2Ti_3O_7$ have also been studied as anodes in Li-ion and Na-ion batteries, which suggests potassium titanium oxide and its analogues could be suitable for KIB negative electrodes.[3]

Studies on $K_2Ti_4O_9$, $KTiOPO_4$, and $KTi_2(PO_4)_3$ have been carried out. These negative materials have not been studied in all-solid state KIBs. The synthesis of these materials have been carried out using solid-state and hydrothermal methods. Fundamental characterizations, including PXRD, SEM, and EDX, have been used to check the crystal structure, phase purity, morphology, and atomic structure of the samples. These materials have also been cycled in potassium half-cells with different conventional and PEO-KTFSI polymer solid electrolytes. Based on cycling results obtained so far, $K_2Ti_4O_9$ shows a good discharge capacity in both conventional and polymer solid electrolytes.

References

[1] A. D. Khudyshkina, P. A. Morozova, A. J. Butzelaar, M. Hoffmann, M. Wilhelm, P. Theato, S. S. Fedotov and F. Jeschull, *ACS Applied Polymer Materials*, 2022, **4**, 2734–2746.

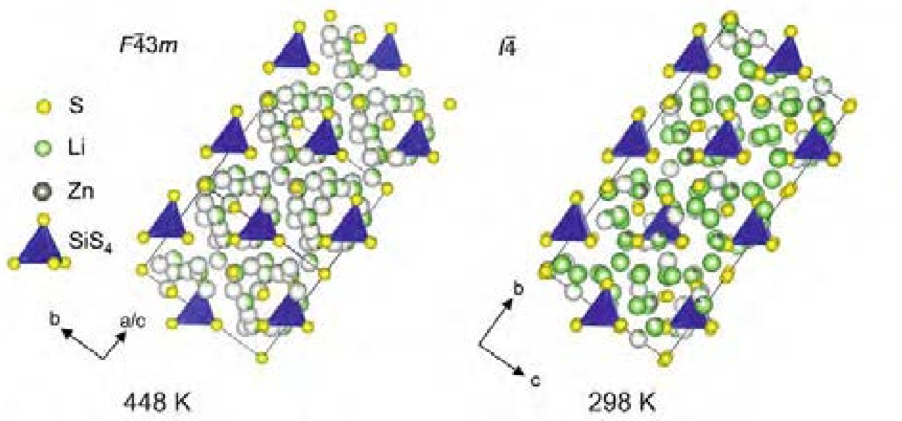
[2] B. Kishore, Venkatesh G and N. Munichandraiah, *Journal of The Electrochemical Society*, 2016, **163**, A2551.

[3] M. Sha, L. Liu, H. Zhao and Y. Lei, *Carbon Energy*, 2020, **2**, 350–369.

Cation Disorder and Large Tetragonal Supercell Ordering in the Li-rich Argyrodite Li$_7$Zn$_{0.5}$SiS$_6$[1]

Bernhard T. Leube,[1] Christopher M. Collins,[1] Luke M. Daniels,[1] Benjamin B. Duff,[1,2] Yun Dang,[1] Ruiyong Chen,[1] Michael W. Gaultois,[1,3] Troy D. Manning,[1] Frédéric Blanc,[1,2,3] Matthew S. Dyer,[1,3] John B. Claridge,[1,3] Matthew J. Rosseinsky[1,3]

[1] Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD, Liverpool, UK
[2] Stephenson Institute for Renewable Energy, University of Liverpool, Peach Street, L69 7ZF, Liverpool, UK
[3] Leverhulme Research Centre for Functional Materials Design, Materials Innovation Factory, Oxford Street, L7 3NY, UK



High temperature (448K) and room temperature (298K) structures of Li$_7$Zn$_{0.5}$SiS$_6$

A tetragonal argyrodite with >7 mobile cations, Li$_7$Zn$_{0.5}$SiS$_6$, is experimentally realized for the first time through solid state synthesis and exploration of the Li-Zn-Si-S phase diagram. The crystal structure of Li$_7$Zn$_{0.5}$SiS$_6$ was solved *ab initio* from high-resolution X-ray and neutron powder diffraction data and supported by solid-state NMR. Li$_7$Zn$_{0.5}$SiS$_6$ adopts a tetragonal $I\bar{4}$ structure at room temperature with ordered Li and Zn positions and undergoes a transition above 411.1(5) K to a higher symmetry disordered $F\bar{4}3m$ structure more typical of Li-containing argyrodites. Simultaneous occupation of four types of Li site (T5, T5a, T2, T4) at high temperature and five types of site (T5, T2, T4, T1, and a new trigonal planar T2a position) at room temperature is observed. This combination of sites forms interconnected Li pathways driven by the incorporation of Zn^{2+} into the Li sublattice and enables a range of possible jump processes. Zn^{2+} occupies the 48*h* T5 site in the high-temperature $F\bar{4}3m$ structure, and a unique ordering pattern emerges in which only a subset of these T5 sites are occupied at room temperature in $I\bar{4}$ Li$_7$Zn$_{0.5}$SiS$_6$. The ionic conductivity, examined via AC impedance spectroscopy and VT-NMR, is 1.0(2) × 10^{-7} S cm^{-1} at room temperature and is 4.3(4) × 10^{-4} S cm^{-1}at 503 K. The transition between the ordered $I\bar{4}$ and disordered $F\bar{4}3m$ structures is associated with a dramatic decrease in activation energy to 0.34(1) eV above 411 K. The incorporation of a small amount of Zn^{2+} exercises dramatic control of Li order in Li$_7$Zn$_{0.5}$SiS$_6$ yielding a previously unseen distribution of Li sites, expanding our understanding of structure-property relationships in argyrodite materials.

References

1. B. T. Leube, C. M. Collins, *et al.* Cation Disorder and Large Tetragonal Supercell Ordering in the Li-Rich Argyrodite Li$_7$Zn$_{0.5}$SiS$_6$, ***Chemistry of Materials***, **2022**, **34**, 4073-4087.10.1021/acs.chemmater.2c00320

Oxide Ion Diffusion Mechanism in Melilite from ^{17}O Variable Temperature MAS and ^{71}Ga MAS NMR

Lucia Corti,[1,2] Matthew J. Rosseinsky[1,2] and Frédéric Blanc.[1,2,3]

[1] Department of Chemistry, University of Liverpool, UK,

[2] Leverhulme Research Centre for Functional Materials Design, University of Liverpool, UK,

[3] Stephenson Institute for Renewable Energy, University of Liverpool, UK.

The design of novel fast oxide ion conductors that exhibit elevated oxide ion conductivity in the intermediate temperature range between 600 °C and 800 °C is crucial for the development of efficient solid oxide fuel cells. A fast oxide ion conductor with $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ composition and melilite structure has attracted research interest owing to its remarkably high ionic conductivity reaching values between 0.02 Scm^{-1} and 0.1 Scm^{-1} in the 600 °C – 900 °C temperature range[1]. In this work, insight into the structural differences between the poorly conductive $LaSrGa_3O_7$ and the highly conductive $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ melilite phases is gained from ^{17}O and ^{71}Ga Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) experiments. Furthermore, the local dynamics in the melilite phases is probed with ^{17}O Variable Temperature (VT) MAS NMR up to 600 °C. The assignment of the complex spectral line shapes observed in the ^{17}O and ^{71}Ga MAS NMR spectra of the disordered melilite phases is guided by the computation of the NMR parameters using the Gauge-Including Projector Augmented Wave (GIPAW) approach[2] on an ensemble of symmetrically inequivalent configurations generated using the Site-Occupation Disorder (SOD) program[3]. Notably, the ^{17}O MAS NMR spectrum of $La_{1.54}Sr_{0.46}Ga_3{}^{17}O_{7.27}$ displays one strongly deshielded signal which is not observed for $LaSrGa_3{}^{17}O_7$. This signal is assigned to interstitial defects which form as $LaSrGa_3O_7$ is doped with La^{3+} to form $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$. Furthermore, a five-coordinate Ga site which forms to accommodate the interstitial defects is probed in the ^{71}Ga Hahn echo MAS NMR spectrum of $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$. Finally, coalescence of all the signals in the ^{17}O VT MAS NMR spectra of $La_{1.54}Sr_{0.46}Ga_3{}^{17}O_{7.27}$ indicates the occurrence of chemical exchange between the oxide ions, thereby implying the possible participation of all oxide ions in the diffusion mechanism under the assumption that the dynamics probed leads to long-range conduction.

References

[1] X. Kuang, M. A. Green, H. Niu, P. Zajdel, C. Dickinson, J. B. Claridge, L. Jantsky and M. J. Rosseinsky, *Nat. Mater.* **2008**, *7*, 498-504.

[2] C. J. Pickard, F. Mauri, *Phys. Rev. B* **2001**, *63*, 2451001.

[3] R. Grau-Crespo, S. Hamad, C. R. A. Catlow, N. H. de Leeuw, *J. Phys. Condens. Matter* **2007**, *19*, 256201.

Defect Chemistry and Ion Transport in Low-Dimensional-Networked Li-Rich Anti-Perovskites as Solid Electrolytes for Solid-State Batteries

Ana Carolina Coutinho Dutra,[1] James A. Dawson[1,2]

[1] Chemistry – School of Natural and Environmental Sciences, Newcastle University,
Newcastle upon Tyne, NE1 7RU, UK,

[2] Centre for Energy, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK,

Face the current climate emergency, solid-state batteries have been attracting significant attention due to a plethora of potential advantages, such as energy density gains, reduced costs, and safety enhancements.[1] In recent years, Li-rich anti-perovskites have stood out as promising solid electrolyte candidates as they combine high ionic conductivity, stability against Li metal anodes and structural versatility.[2]

Here, defect simulations are used to explore the energetics of defect formation in a range of Li_xOX_y (X = Cl or Br; x = 3–6; y = 1–4) anti-perovskites with zero- to three-dimensional structures. Defect calculations are conducted utilising the Mott−Littleton approximation. Long molecular dynamics runs are carried to assess ion transport in these materials at a range of temperatures (200–800 K). The range of defects investigated includes full, Li-halide and Li-O Schottky defects and Li Frenkel defects. Our calculations predict that whereas almost all these materials present Li-halide Schottky defect pairs as dominant native defects, Cl interstitials are the dominant type of intrinsic disorder in Li_6OCl_4. We find that the formation of the great majority of defect types is energetically more favourable in the Li_xOCl_y series compared to the equivalent structures in the Li_xOBr_y set, potentially leading to enhanced Li-ion transport in these materials. We also report that the concentrations of halide Frenkel defects in the Li_xOBr_y set are lower than expected in the three and two-dimensional structures, based on the Li_xOCl_y series findings for their counterparts. Our molecular dynamics simulations reveal the strong connection between Li-ion dynamics and dimensionality in these anti-perovskite materials, where increased Li-ion diffusion and decreased activation energy can be seen as dimensionality is reduced. Density functional theory simulations and machine learning studies are currently ongoing to further assess ion transport and interfaces in these materials.

References

[1]T. Famprikis, P. Canepa, J. A. Dawson, M. S. Islam and C. Masquelier, *Nature Materials*, 2019, **18**, 1278.

[2]J. A. Dawson, T. Famprikis and K. Johnston, *Journal of Materials Chemistry A*, 2021, **9**, 18746.

Computational Discovery of Charge-ordered Ferroelectrics

Dan Criveanu[1] and Katherine Inzani.[1]

[1] School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK.

Ferroelectric materials are vital for many technological applications such as SONAR and ultrasonic transducers, owing to their spontaneous, switchable electric dipole. However, new ferroelectrics are needed to facilitate emerging applications, for example memristors for neuromorphic computing,[1,2] for which ideal ferroelectrics have not been found.[3] A particular subset of ferroelectrics are driven to a net dipole moment by charge ordering (CO) on atom sites and bonds.[4] These CO-driven ferroelectrics have largely evaded high-throughput computational searches due to the difficulty in capturing CO accurately with standard *ab initio* techniques. Here, we design a materials database search to identify improbable structures that would likely stabilize by CO. Our search has revealed 14 potential CO structures, and we use spin-polarised density functional theory (DFT) calculations to further explore two of these, $Li_6Bi_2O_7$ and $Li_6Sb_2S_7$. Symmetry unconstrained structure relaxations gave rise to a polar phase for $Li_6Bi_2O_7$ that shows evidence of checkerboard-type CO. This work identifies $Li_6Bi_2O_7$ as a new CO ferroelectric candidate. Utilization of these materials informatics techniques aims to expand the pool of known compounds with CO-driven polar transitions, improving understanding of this special class of material and uncovering new ferroelectric candidates.

References

[1] S. H. Jo et al., Nano Lett., 2010, **10**, 1297–1301.
[2] A. Chanthbouala et al., Nat. Mater., 2012, **11**, 860–864.
[3] J. Guo et al., Appl. Phys. Lett., 2020, **117**, 262903.
[4] S. Y. Park et al., Proc. Natl. Acad. Sci., 2019, **116**, 23972.

Developing a Solvothermal Reaction Cell for *in situ* Neuron Scattering of Crystallisation

Mark Crossman,[1] Helen Y. Playford,[2] and Richard I. Walton.[1]

[1] Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom,

[2] ISIS Facility Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom

Despite solvothermal synthesis being one of the most versatile methods for the synthesis of metal oxides, little is known of the chemistry that occurs during the process due to the closed nature of a solvothermal reaction. Although a range of X-ray techniques have been used to follow solvothermal crystallisations, the benefits of neutron diffraction have not been exploited in the *in situ* sudy of the formation of materials. This includes the penetration of bulky reaction vessels, sensitivity to low atomic number elements, and, potentially, study of magnetic materials.

In this contribution I will explore the potential of a new cell design which is composed of a null-scattering titanium zirconium alloy ($Ti_{0676}Zr_{0.324}$) with an aim for the cell to be easily transportable and adaptable to a variety of neutron instruments depending on suitability for the reactions being studied. The cell has been deployed in the study of the synthesis of the strontium ruthenate $SrRu_2O_6$ on POLARIS at ISIS for the real time monitoring of its crystallization at different temperatures. This material is of particular interest for its potential as a new semiconductor material while also possessing antiferromagnetic ordering with a Néel point above the synthesis temperature (T_N = 565 K). It has also been reported that with minor changes to the synthesis conditions of $SrRu_2O_6$, two additional strontium ruthenate phases can be produced. This makes the study of this material ideal to explore the potential of the cell in monitoring synthesis routes, magnetic structure formation in real time and reaction kinetics. The cell has also been used to study the formation of zeolite A (LTA) and its conversion under basic conditions to hydrosodalite (SOD) on NIMROD at ISIS. This allows for studying the impact of temperature on the rate of formation of the zeolite and the rate of conversion to the sodalite with an opportunity to use the cell to study disordered materials and its suitability for PDF analysis *in situ.*

Discovery of a new lithium ion conductor in the Li-Mg-Al-P-O phase field

Yun Dang, Guopeng Han, Elvis Shoko, Matthew Dyer, Luke Daniels, John Claridge, Matthew Rosseinsky

Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK

All-solid-state batteries are a promising avenue to significantly advance lithium ion battery technology, particularly for electric vehicle applications. In order to search for new lithium oxide materials suitable for solid electrolyte applications, we selected a quinary oxide material system consisting of light elements, Li-Mg-Al-P-O, motivated by the desire for a light electrolyte. A new lithium metal phosphate, $Li_{1.76}Mg_{0.62}Al_2P_9O_{27}$, was discovered through the computationally guided synthetic exploration. The crystal structure was solved via single crystal X-ray diffraction, and adopts the hexagonal space group $P6_3/mcm$ with $a = b = 10.9981(5)$ Å and $c = 9.3530(9)$ Å. The structure can be descried as a three-dimensional framework of MO_6 and PO_4 units, of which the connectivity is similar to NASICON with extended packing. The structure also affords a straight and wide channel along the *c* axis, which is occupied by Li^+ cations. Phase-pure powder samples were synthesized successfully at 873 K for 40 h. The homogeneity and crystallinity of samples were confirmed via TEM, and the lithium ionic conductivity was examined via AC impedance spectroscopy. $Li_{1.76}Mg_{0.62}Al_2P_9O_{27}$ is the first quaternary lithium compound found in the phase field, and more structural and property diversities may be possible to access from innovative doping of the new hexagonal structure.

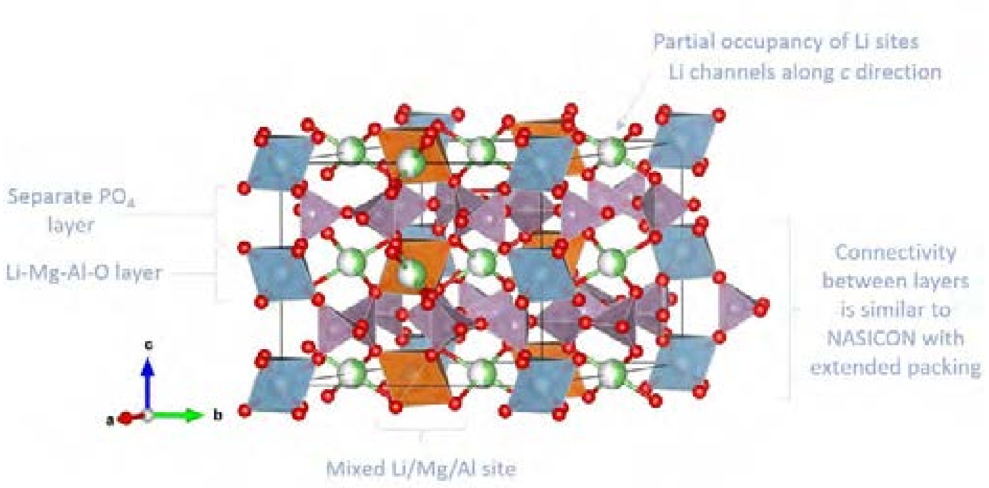


Figure 1. Crystal structure of $Li_{1.76}Mg_{0.62}Al_2P_9O_{27}$

High-performance protonic ceramic fuel cell cathode using protophilic mixed ion and electron conducting material

Dingyue Hu,[1] Junyoung Kim,[1] Hongjun Niu,[1] Luke M. Daniels,[1] Troy D. Manning,[1] Ruiyong Chen,[1] Bowen Liu,[1] Richard Feetham,[1] John B. Claridge[1] and Matthew J. Rosseinsky[1]
[1] Department of Chemistry, Materials Innovation Factory, University of Liverpool, 51 Oxford Street, Liverpool, UK

Ceramic fuel cells are considered to be eco-friendly alternative devices for energy production due to their high energy conversion efficiencies and continuous electricity production without polluting emissions.[1] Protonic ceramic fuel cells (PCFCs) are promising candidates for intermediate to low temperature operation (400-600 °C), in contrast to solid oxide fuel cells which typically operate at 800 °C. Widespread application of PCFCs relies on the development of high-performance electrode materials.

We report on a self-assembled nanocomposite, $Ba_{0.5}Sr_{0.5}(Co_{0.7}Fe_{0.3})_{0.6875}W_{0.3125}O_{3-\delta}$ (shortened to BSCFW),[2] and its electrochemical and protonic properties in the context as a PCFC cathode material.[3] BSCFW is a nanocomposite consisting of a disordered single perovskite with high electrocatalytic activity, and an electronically conducting oxygen-stoichiometric ordered double perovskite phase.

BSCFW has an excellent polarisation resistance (R_p) of 0.172(2) Ω cm^2 at 600 °C and a high power density of 582(1) mW cm^{-2} through single cell measurement which is comparable with current state-of-the-art cathode materials. It displays good chemical and thermal stability against a $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) electrolyte with a low R_p degradation rate of 1.01(1) × 10^{-6} Ω cm^2 min^{-1}. This performance is improved beyond the well-studied $Ba_{0.5}Sr_{0.5}Co_{0.7}Fe_{0.3}O_{3-\delta}$ (BSCF) type materials, which tend to be unstable under the same conditions and incompatible with the electrolyte material. The high performance and stability presented by BSCFW is determined via the interplay of the single and double perovskite phases.

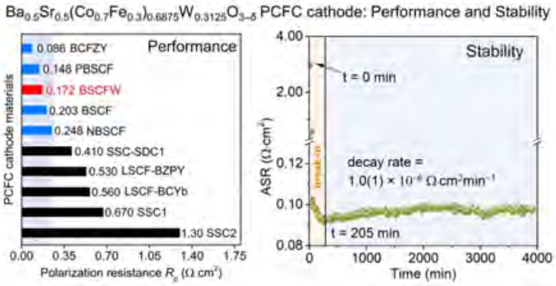


Figure 1: Comparison (left) of R_p of BSCFW (red) with other representative PCFC cathode materials at 600 °C. ASR stability (right) of a BSCFW|BZCYYb|BSCFW symmetrical cell in 3 vol% hydrated air at 600 °C.

References

[1] S. Sengodan, S. Choi, A. Jun, T. H. Shin, Y.-W. Ju, H. Y. Jeong, J. Shin, J. T. Irvine and G. Kim, *Nat. Mater.*, 2015, **14**, 205.

[2] J. F. Shin, W. Xu, M. Zanella, K. Dawson, S. N. Savvin, J. B. Claridge and M. J. Rosseinsky, *Nat. Energy*, 2017, **2**, 16214.

[3] D. Hu, J. Kim, H. Niu, L. M. Daniels, T. D. Manning, R. Chen, B. Liu, R. Feetham, J. B. Claridge and M. J. Rosseinsky, *J. Mater. Chem. A*, 2022, **10**, 2559.

[4] N. Bausá, C. Solís, R. Stranbakke and J. M. Serra, *Solid State Ionics*, 2017, **306**, 62.

Thermal expansion and phase transitions in niobium oxyfluorides

Eliza K. Dempsey[1] and James Cumby

[1]School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ.

The control of thermal expansion is key for any engineering materials which undergo significant temperature changes, for instance by improving thermal shock resistance or reducing strain in solid oxide fuel cells.[1, 2] ReO_3-type structures, such as ScF_3, can exhibit negative thermal expansion through thermally-induced octahedral tilting (Fig. 1).[3] Many ReO_3-type trifluorides and oxyfluorides also show an octahedral tilting pressure phase transition, from Pm-3m to R-3c.[4] The octahedral tilting, therefore, creates a clear link between the temperature-pressure behaviour of ReO_3-type structures.[5]

The variable oxidation state of niobium in NbO_2F allows the formation of a ReO_3-type oxygen-fluorine solid solution.[6] This provides an excellent model system for exploring the impact of anionic composition on physical properties which has so far been overlooked.

A full pressure-temperature phase diagram for both pure and fluoride-doped NbO_2F has been established through x-ray diffraction. Fluorine doping of NbO_2F is found to induce negative thermal expansion and significantly influence the lattice dynamics. Combining ab initio predictions with x-ray diffraction at extreme conditions provides insight into the fundamental relationship between anionic composition, thermal expansion and pressure phase transitions. This presents a new pathway for the design of functional mixed-anion materials with controllable pressure and temperature responses.

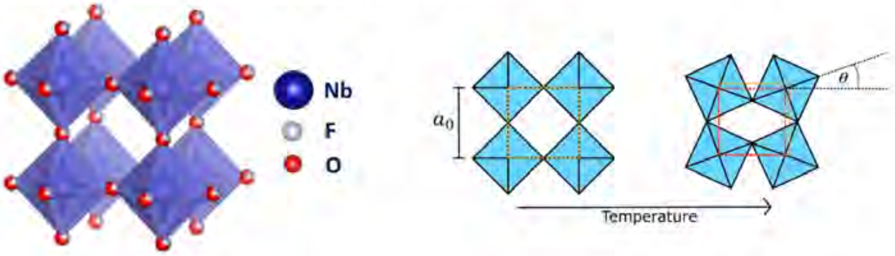


Figure 1: (a) Structure of cubic NbO_2F (b) Model for negative thermal expansion from rigid octahedral tilting modes.

References

1. J. Chen, L. Hu, J. Deng and X. Xing, *Chem. Soc. Rev.*, 2015, **44**, 3522-3567.
2. J.-H. Kim and A. Manthiram, *Chem. Mater.*, 2010, **22**, 822-831.
3. B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas, K. W. Chapman and A. P. Wilkinson, *Journal of the American Chemical Society*, 2010, **132**, 15496-15498.
4. S. Carlson, *J. Appl. Crystallogr.*, 2000, **33**, 1175-1176.
5. C. R. Morelock, L. C. Gallington and A. P. Wilkinson, *J. Solid State Chem.*, 2015, **222**, 96-102.
6. F. J. Brink, L. Norén and R. L. Withers, *J. Solid State Chem.*, 2004, **177**, 2177-2182.

Ionic liquids and operando photoemission spectroscopy

Avishek Dey,[1] Roxanna Lee, Tim Nunney[2] and Robert Palgrave.[3]

[1] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom

[2]Thermo Fisher Scientific, Surface Analysis, Unit 24, The Birches Industrial Estate, East Grinstead, West Sussex, RH19 1UB, United Kingdom

Various energy storage devices are being widely used from consumer electronics. However, to improve efficiency and performance of these devices it is important to understand the fundamental processes occurring in each component of the battery. During the first charge/discharge cycle of the battery a solid electrolyte interphase (SEI) is formed from the breakdown of dissolved salts in the electrolyte. Due to the ultra-high vacuum environment in standard X-ray instruments it is a challenge to perform operando surface analysis of battery components.

Ionic liquid (IL) with their superior thermal stability, large electrochemical window, and negligible flammability are promising substitutes to organic electrolytes. Critically, low vapour pressure of ILs enables them to be studied under UHV environments.[1–3] Use of IL will allow integration of traditional battery fabrication units with standard XPS instruments. In batteries the key factor controlling the device performance is the chemical interaction between electrode and electrolyte during charging and discharging. This work is aimed at tuning the chemistry of ILs and understanding their properties using X-ray photoelectron spectroscopy. Along with looking at their application in operando studies of electrochemical processes. Room temperature ionic uids RTILs are molten salts with a weekly coordinated cation and anion. The extremely low vapour pressure is one of the extraordinary properties of room temperature ionic liquids (RTILs). This work comprises of tuning the chemistry of ILs and characterising their properties using X-ray photoelectron spectroscopy. Along with looking at their application in operando studies of electrochemical processes.[4]

Through core level and valence band measurements we have found that cation symmetry and the length of alkyl chain influence their spectral signature. For cations with short chain alkyl groups the valence band is dominated by the anion.[5] While with longer alkyl chain the cation starts to influence the valence band structure. Moreover, a linear increase in work function is also observed when the alkyl groups is increased form butyl to hexyl to octyl. RTILs being electrochemically inert provide an opportunity for operando studies of electrochemical properties. We used these properties of RTILs to probe the surface chemistry of SEI i.e the electrode electrolyte interfaces during operation.

References

1 K. Matsumoto, J. Hwang, S. Kaushik, C. Y. Chen and R. Hagiwara, *Energy Environ Sci*, 2019, **12**, 3247–3287.

2 D. A. Rakov, F. Chen, S. A. Ferdousi, H. Li, T. Pathirana, A. N. Simonov, P. C. Howlett, R. Atkin and M. Forsyth, *Nat Mater*, 2020, **19**, 1096–1101.

3 J. Sun, L. A. O'Dell, M. Armand, P. C. Howlett and M. Forsyth, *ACS Energy Lett*, 2021, 2481–2490.

4 Z. Liu, O. Höfft, A. S. Gödde and F. Endres, *Journal of Physical Chemistry C*, 2021, **125**, 26793–26800.

5 J. M. Seymour, E. Gousseva, A. I. Large, C. J. Clarke, P. Licence, R. M. Fogarty, D. A. Duncan, P. Ferrer, F. Venturini, R. A. Bennett, R. G. Palgrave and K. R. J. Lovelock, *Physical Chemistry Chemical Physics*, 2021, **23**, 20957–20973.

Magnetocaloric Studies of a Family of Ln Adipate Metal-Organic Framework Materials

Patrick W. Doheny,[1] Simon J. Cassidy[2] and Paul J. Saines[1]

[1] School of Physical Sciences, Ingram Building, University of Kent, Canterbury, CT2 7NH, UK,

[2] Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, UK

Low temperature cooling applications below 80 K such as quantum computing, hydrogen liquefaction and medical imaging techniques are underlined by a dependence on liquid helium, an expensive and finite resource. The development of new low temperature cooling materials, such as those utilising magnetic refrigeration, is therefore an active area of research with the end goal of replacing liquid helium with sustainable solid-state materials. Magnetocaloric materials, in which low temperature cooling is achieved by changes in magnetic entropy upon the cycling of an applied magnetic field, require high densities, rapid magnetisation at low applied fields and the suppression of long-range magnetic ordering to achieve optimal refrigeration properties.

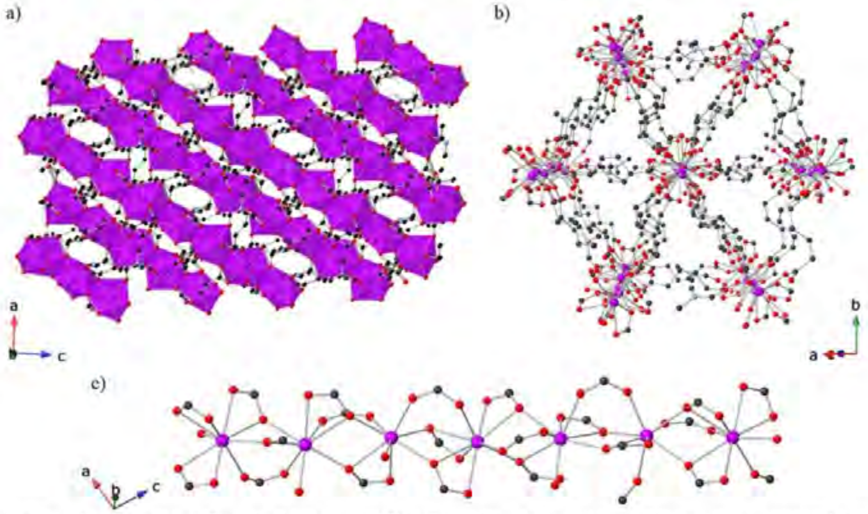


Figure 1. Crystal structure of $Gd_3(adipate)_{4.5}(DMF)_2$ showing a) the *ac*-plane in which large positive and negative thermal expansion occurs, b) the distorted triangular pores and c) the extended Gd chain.

Metal-Organic Frameworks (MOFs) are one class of material that can satisfy these design criteria with the choice of magnetic ion and organic ligand allowing access to dense structures with tuneable magnetic properties. This presentation will detail the study of the magnetocaloric and thermal expansion properties of the $Ln_3(adipate)_{4.5}(DMF)_2$ (Ln = Gd-Er) family of frameworks in which 1D Ln chains are crosslinked by flexible adipate ligands to form an extended 3D network.[1] Utilising magnetic measurements, the magnetic entropy changes of these materials between 2-10 K were calculated, with the Gd material achieving the highest magnetic entropy change of 36.4 J kg^{-1} K^{-1} at 2 K for a 5-0 T field change while the Er phase performed better at lower fields due to the presence of ferromagnetic Er chains within the structure. Single crystal X-ray diffraction was also used to study the thermal expansion properties over a 100-300 K temperature range. The materials exhibit anomalous thermal expansion properties with anisotropic negative thermal expansion and colossal positive thermal expansion shown by several members of the series that was attributed to a framework hinging mechanism.

References

[1] P. W. Doheny, S. J. Cassidy and P. J. Saines, *Inorg. Chem.*, 2022, **61**, 4957.

Tuning Intra- and Inter-plane Exchange Interactions in Two-Dimensional *S* = ½ Kagome Metal-Organic Frameworks

T. N. Dolling, S. Ivko, and L. Clark

School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

The applications of magnetic *S* = ½ kagome materials range from the long-sought quantum spin liquid, to low-energy data storage, spintronics, logic gates and quantum computing.[1,2] In recent work,[3] we uncovered the magnetic ground state of a family of *S* = ½ kagome-containing metal-organic frameworks (MOFs) with the general formula $Cu_3(CO_3)_2(x)_3 \cdot 2ClO_4$. In these materials, Cu^{2+} cations are chelated by carbonate anions forming kagome layers in the *ab* plane (Figure 1c) that are pillared along the *c* axis by ditopic organic linkers, *x* = 1,2-bis(4-pyridyl)ethane (*bpe*), 1,2-bis(4-pyridyl)ethylene (*bpy*), or 4,4′-azopyridine (*azpy*). Following the discovery of three-dimensional magnetic order in these MOFs, our attention has turned to two new systems with the formula $Cu_3(CO_3)_2(y)_6 \cdot 2ClO_4$ where *y* is 4-methylpyridine (*mp*) or 2,4'-bipyridine (*bipy*). Substituting the pillaring linkers used previously for these monodentate ligands effectively removes the interplane covalent linkage, which, it is expected, will disrupt the three-dimensional ordering observed in the pillared systems. At the same time, we are exploring the effects of substituting the in-plane linkers, in particular, hexahydroxybenzene (*hhb*), in which we show that the Cu-Cu exchange pathways are altered. Intriguingly, exchange is ferromagnetic through the carbonate linker and antiferromagnetic through *hhb* according to our magnetometry data, highlighting the tunability offered through two-dimensional magnetic MOFs (Fig. 1b). Furthermore, the discrete layers in these structures (Fig. 1a) may also allow for the exfoliation of these MOFs into magnetic nanosheets, which have a plethora of potential applications including as ultrathin semiconductors and spin valves.[4,5] Work on understanding the synthesis, crystal structures and magnetic properties of these systems, as well as preliminary studies on their exfoliation will be presented herein.

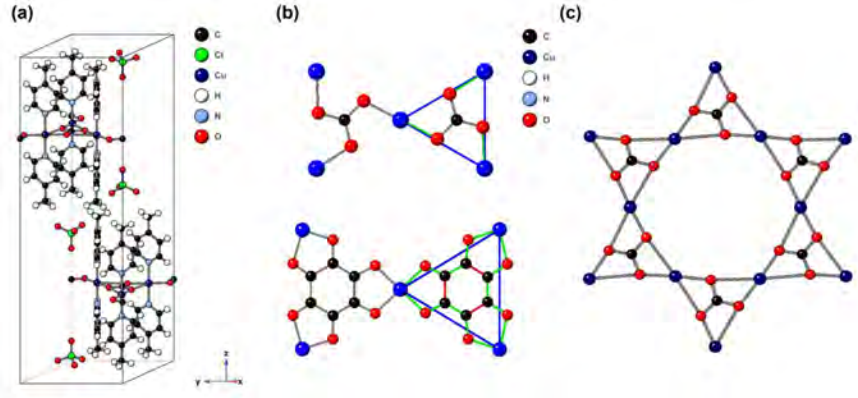


Figure 4. *Structural models of MOF-mp (a) The unit cell of MOF-mp solved in the $P6_3/m$ space group. (b) Comparison of magnetic copper environments in both (top) MOF-mp and (bottom) MOF-HHB species wherein there is no interplane linkage along the c axis (c) The kagome lattice of MOF-mp featuring a network of Cu^{2+} cations chelated by CO_3^{2-} anions (perchlorate anions omitted).*

References: [1]A. Fert, N. Reyren, and V. Cros, Nature Reviews Materials, (2017), 2, 17031. [2]G. Hu and B. Xiang, Nanoscale Research Letters (2020), 15, 226. [3]S. A. Ivko. et. al, Chemistry of Materials (2022), 34, 5409. [4]K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Physical Review Letters (2010), 105, 136805. [5]Z. Wang, D. Sapkota, T. Taniguchi, K. Watanabe, D. Mandrus, and A. F. Morpurgo, Nano Letters (2018), 18, 4303.

Synthesis, Structure and Electrochemical Properties of a New Cation Ordered Layered Li-Ni-Mg-Mo Oxide

Bo Dong[*,1,2], Javier Castells-Gil[1,2], Pengcheng Zhu[2,3], Laura L. Driscoll[1,2], Emma Kendrick[2,3], Phoebe K. Allan[1,2], Peter R. Slater[*,1,2]

[1] School of Chemistry, University of Birmingham, Birmingham B15 2TT, U.K.
[2] The Faraday Institution, Harwell Science and Innovation Campus, Didcot OX11 0RA, U.K.
[3] School of Metallurgy and Materials, University of Birmingham, Birmingham B15 2TT, U.K.

To meet the demand in the growing electrical energy storage, such as electric vehicles and grid storage applications, novel cathode materials with large storage capacity and high energy density are required. Lithium-rich oxides are attracting intense interest as the next generation cathode materials for lithium-ion batteries due to their high theoretical capacity[1-3]. Nevertheless, these materials suffer from a number of shortcomings, such as oxygen loss at high voltage, large hysteresis and poor rate capability. In this work, we show that through a dual cation doping strategy replacing Ti with Mo and Mg, the disordered rocksalt (DRS) $Li_{1.2}Ni_{0.4}Ti_{0.4}O_2$ is transformed into a new cation ordered layered phase $Li_{1.2}Ni_{0.4}Mo_{0.2}Mg_{0.2}O_2$, with the high valence dopant Mo^{6+} on the (0,0,0) site. $Li_{1.2}Ni_{0.4}Mo_{0.2}Mg_{0.2}O_2$ showed improved performance compared to that of the similarly prepared DRS $Li_{1.2}Ni_{0.4}Ti_{0.4}O_2$ material (~190 mAhg^{-1} vs ~105 mAhg^{-1} after 10 cycles, respectively). The characteristics of the electrochemical process were studied using ex situ XRD and XAS, which indicated the involvement of both Ni and Mo redox during the cycling as well as the electrochemical instability of the layered phase which changes to a disordered rocksalt phase on cycling.

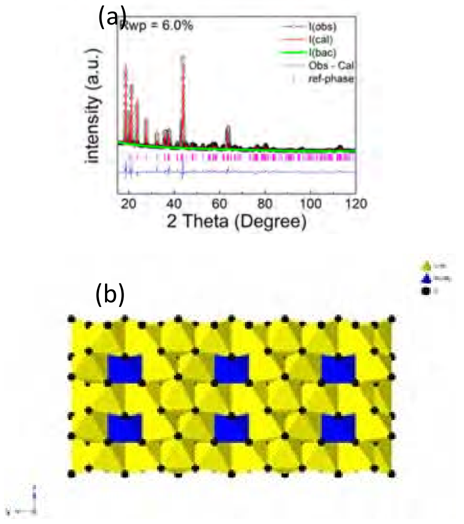


Fig 1. (b) Observed, calculated and difference profiles from structure refinement for $Li_{1.2}Ni_{0.4}Mo_{0.2}Mg_{0.2}O_2$. (c) Structure of $Li_{1.2}Ni_{0.4}Mo_{0.2}Mg_{0.2}O_2$.

References

1 R.A. House, J.-J. Marie, M.A. Pérez-Osorio, G.J. Rees, E. Boivin, P.G. Bruce. *Nat. Energy*, 2021, **6**, 781-789. 2 G. Assat, J.-M. Tarascon, *Nat. Energy*, 2018, **3**, 373-386. 3 J.P. Huang, P.C. Zhong, Y. Ha, D.-H. Kwon, M.J. Crafton, Y.S. Tian, M. Balasubramanian, B.D. McCloskey, W.L. Yang, G. Ceder. *Nat. Energy*, 2021, **6**, 706-714.

Vacancy-Regulated Charge Carrier Dynamics and Suppressed Nonradiative Recombination in Two-dimensional ReX_2 (X=S, Se)

Wenzhen Dou,[1,2] Miao Zhou[1]

[1] School of Physics, Beihang University, Beijing 100191, China

[2] Present Address: Department of Chemistry, University College London, 20 Gordon
Street, London WC1H 0AJ, United Kingdom

Point defects in semiconductors usually act as nonradiative charge carrier recombination centers, which severely limit the performance of optoelectronic devices. In this work, by combining time-domain density functional theory with nonadiabatic molecular dynamics simulations, we demonstrate suppressed nonradiative charge carrier recombination and prolonged carrier lifetime in two-dimensional (2D) ReX_2 (X = S, Se) with S/Se vacancies. In particular, S vacancy introduces a shallow hole trap state in ReS_2, while Se vacancy introduces both hole and electron trap states in $ReSe_2$. Photoexcited electrons and holes can be rapidly captured by these defect states, while the release process is slow, which contributes to an elongated photocarrier lifetime. The suppressed charge carrier recombination lies in the vacancy-induced low-frequency phonon modes that weaken electron-phonon coupling, as well as the reduced overlap between electron and hole wavefunctions that decreases nonadiabatic coupling. This work provides physical insights into the charge carrier dynamics of 2D ReX_2, which may stimulate considerable interest in using defect engineering for future optoelectronic nanodevices.

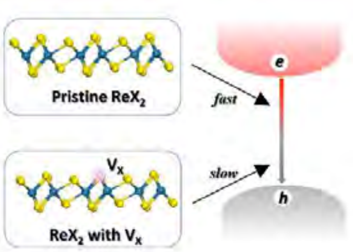


Figure 1. The schematic of electron-hole recombination in pristine ReX_2 and defective ReX_2.

References

[1] W. Z. Dou et al., *J. Phys. Chem. Lett.* 2022, **13**, 10656−10665.

Building Upon the Blocks of Battery Technology:

Further Resource Development from the Birmingham Battery Bunch

Elizabeth H. Driscoll[1,4], Zoë H. Wright[2,4], Emily Hanover[2,4], Sophia Constantinou[4], Tabitha Seymour[2,4], Gagandeep Nandera[2,4], Pooja Goddard[3], Emma Kendrick[1,4], Peter. R. Slater[2,4]

[1] School of Metallurgy and Materials, The University of Birmingham, Edgbaston, B15 2SE, UK

[2] School of Chemistry, The University of Birmingham, Edgbaston, B15 2TT, UK

[3] Sir David Davies Building, Loughborough University, Loughborough, LE11 3TD, UK

[4] The Faraday Institution, Harwell Campus, Didcot, OX11 0RA, UK

Li-ion batteries have remained a hot and important topic since commercialization in the 90's – such that the increased interest for electrification within the automotive industry has had its own media "thermal" runaway, with the dream of purchasing an electric vehicle becoming more of a reality, evidenced by the increased visibility in society. With the current UK policy direction towards Net Zero and limiting the sale of new internal combustion engines by 2030, there needs to be more open sources which communicate this technology – which goes beyond the two equations on Li-ion batteries within the A level Chemistry curriculum[1], to not only engage with the science but to inspire the next generation of scientists. This priority within the Chemistry curriculum towards the education upon climate change and sustainability has been recognised within the Royal Society of Chemistry's (RSC) "Green shoots: A sustainable chemistry curriculum for a sustainable planet" report.[2]

To support learning and be engaging, hands-on demonstrations are often used. The most commonly used activity employs lemon cells[3], which are useful for introducing the concept of electrode potentials, electrical circuits and a non-rechargeable battery. It is difficult to not mention efforts by Prof. Saiful Islam in battery engagement with this activity, with the lemon battery's cameo in the 2016 Royal Institution Christmas Lectures and more recently achieving a Guinness World Record, in collaboration with the RSC to achieve a battery delivering 2,307.8 V (with a current of 0.84 mA).[4,5] Hence, without a doubt this practical is well established and can be used as a practical and safe demonstration.

However towards exploring Li-ion battery operation, limited resources are available. Within this talk "Battery Jenga" will be initially presented[6], along with new resources produced from the Birmingham Battery Bunch, which will explore: synthesis, manufacture, fabrication, and recycling of Li-ion batteries in resource form, as well as highlighting "Behind the Lab Specs" - a video series exploring the variety of battery careers which don't necessarily involve a lab coat![7]

References

1 AQA AS and A-level Chemistry: 7404, 7405: Specification, https://www.aqa.org.uk/subjects/science/as-and-a-level/chemistry-7404-7405/subject-content/physical-chemistry#Electrode_potentials_and_electrochemical_cells_A-level_only, (accessed 2 November 2022).

2 Royal Society of Chemistry: Green shoots : A sustainable chemistry curriculum for a sustainable planet, https://www.rsc.org/new-perspectives/sustainability/a-sustainable-chemistry-curriculum/, (accessed 30 June 2022).

3 S. G. Cady, *J. Chem. Educ.*, 2014, **91**, 1675–1678.

4 Saiful Islam, https://www.rigb.org/explore-science/explore/person/saiful-islam, (accessed 30 May 2022).

5 Highest voltage from a fruit battery, https://www.guinnessworldrecords.com/world-records/108028-highest-voltage-from-a-fruit-battery#:~:text=The highest voltage from a,a power of 1.94 Watts., (accessed 30 May 2022).

6 E. H. Driscoll, E. C. Hayward, R. Patchett, P. A. Anderson and P. R. Slater, *J. Chem. Educ.*, 2020, **97**, 2231–2237.

7 Peter R. Slater Group Website, https://www.prslaterchem.com/outreach, (accessed 2 November 2022).

A Validated Dataset of Experimentally Measured Li Ion Conductivities

Matthew S Dyer,[1,3] Cameron J. Hargreaves,[1] Michael W. Gaultois,[1,3] Luke M. Daniels,[1] E. J. Watts,[1,3] V. A. Kurlin, [2, 3] M. Moran,[1,3] Y. Dang,[1] R. Morris,[1] A. Morscher,[1] K. Thompson,[1] M. A. Wright,[1] B.-E. Prasad,[1] F. Blanc,[1,3,4] C. M. Collins,[1] C. A. Crawford,[1] B. B. Duff,[1,4] J. Evans,[1] J. Gamon,[1] G. Han,[1] B. T. Leube,[1] H. Niu,[1] A. J. Perez,[1] A. Robinson,[1] O. Rogan,[1,3] P. M. Sharp,[1] E. Shoko,[1] M. Sonni,[1] W. J. Thomas,[1] A. Vasylenko,[1] L. Wang,[1] M. J. Rosseinsky[1,3]

[1] Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD
[2] Department of Computer Science, University of Liverpool, Liverpool, L69 3BX
[3] Leverhulme Research Centre for Functional Materials Design, Materials Innovation Factory, University of Liverpool, Liverpool, L7 3NY
[4] Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool, L69 7ZF

We present a database of 820 experimentally measured Li ion conductivities covering 403 unique chemical compositions.[1] Every entry has been validated by an expert in battery chemistry to ensure that it accurately reports the ionic conductivity measured by AC impedance spectroscopy, the temperature at which it was measured and the composition of the sample. The primary source for each entry is also provided. This database is freely available for non-commercial use at http://pcwww.liv.ac.uk/~msd30/lmds/LiIonDatabase.html.

By assigning each material in the database to a structural family, we are able to map out the space of Li ion conductors and clearly identify clusters of structurally related materials. We are also able to place these Li ion conductors into a full map of all reported solid-state inorganic compounds. We demonstrate that the database can be used as the source of data for supervised machine learning problems, and find that it is possible to train a reliable classifier into high or low ionic conductivity based solely on composition with an accuracy of over 80 %.

We believe that this dataset and the models derived from it represent a practical resource for those working in the solid-state Li ion battery community. More generally, what we have learned from our experience in constructing and validating this dataset will be of benefit to others seeking to construct their own dataset of material properties from experimental data reported in the scientific literature.

A map of the chemical families of compounds in the database, shown as coloured symbols, plotted with all Li containing compositions (black dots) and all compositions (grey dots) in the ICSD.

References

[1] C. J. Hargreaves et al., *npj Computational Materials*, in press

Using magnetic ionic liquids as a lubricant to protect solid interfaces

Tim Evans, Professor Robert Palgrave

University College London

It was estimated famously in 1966 that the cost of friction, wear and corrosion to the UK economy is 1.1-1.4% of GDP.[1] With this, the is an evident need to reduce this value. The field of tribology, derived from Greek, covers lubrication where lubricants themselves can be traced as far back as the 17th century during ancient Egyptian times where olive oil was used to move large stones.

A lubricant can be defined as substance used to help reduce friction between surfaces in mutual contact. The challenge for this body of work is to synthesise a novel magnetic lubricant based on ionic liquids that can act as both a lubricant *and* sealant in a vacuum pump.

Magnetism is a desired feature to help reduce the amount of lubricant required and also act as the sealant to help reduce pressure in the vacuum pump.

The lubricant is based on an Ionic Liquid (IL), which is a salt made up purely of positively and negatively charged ions where the ions themselves are often large which as a result makes them poorly coordinating to make a low melting point liquid.[2] Often termed designer solvents due to their facile nature to change the anion/cation combinations to tailor the IL to specific requirements.

Herein, due to their designer nature magnetic properties of the IL are derived from the anion; not to be confused with competing solutions such as a ferrofluid which is magnetic nanoparticles dissolved in a carrier fluid.

References

1. P. Jost, *Lubrication (Tribology) - A report on the present position and industry's needs*, Department of Education and Science, 1966.
2. M. Freemantle, *An Introduction to Ionic Liquids*, 2009.

An Immediate Room Temperature Synthesis Method to Form a Wide Range of Metal-Organic Frameworks for Photocatalytic Degradation

Ehsan Ezzatpour Ghadim, Richard I. Walton

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

Metal organic frameworks (MOFs) are a class of porous materials with large porosity and often high surface area developed since the early 1990s that provide promising candidates to eliminate the environmental impurities [1, 2]. An immediate room temperature synthesis method is used to synthesise a series of Ce-UiO-66-X (X=NH_2, OH, H, NO_2, COOH) metal-organic frameworks. Ce-UiO-66-X (X=NH_2, OH) were synthesised for the first time, which is challenging because Ce(IV) oxidises NH_2 and OH on the BDC (benzene-1,4-dicarboxylate) linker. This synthetic approach not only develops the tunability of MOFs, but also offers a versatile strategy to introduce a new series of UiO-66 materials with exceptional photocatalytic activities.

SEM (scanning electron microscopy), PXRD (powder X-ray diffraction), DRS/UV-Vis (UV-Vis diffuse reflectance spectroscopy), PL (photoluminescence spectroscopy), TGA (thermogravimetric analysis), and FT-IR (Fourier transform infrared spectroscopy) show that the new MOFs have ultrafine nano size, phase purity, narrow band gap, and minimum recombination rate.

The photocatalytic degradation of four dyes (methylene blue, rhodamine B, Congo red, and alizarin red s) using has been measured by under UV and visible light emissions at room temperature. The Ce-UiO-66-NH_2, Ce-UiO-66-OH, and Ce-UiO-66-H exhibit an extraordinary photocatalytic degradation to decolourise anionic dyes (alizarin red s and Congo red) rapidly between 1 and 3 minutes. They show a good photostability and recyclability with retention of structure confirmed by PXRD.

References

[1] S. Dutta, B. Gupta, S.K. Srivastava, A.K. Gupta, Recent advances on the removal of dyes from wastewater using various adsorbents: a critical review, Materials Advances, 2 (2021) 4497-4531.

[2] A. Çiftlik, T. Günay Semerci, O. Şahin, F. Semerci, Two-Dimensional Metal–Organic Framework Nanostructures Based on 4,4′-Sulfonyldibenzoate for Photocatalytic Degradation of Organic Dyes, Crystal Growth & Design, 21 (2021) 3364-3374.

Carbon Capture and Usage: A Study of Na-doped Hydroxyapatite

Elisabeth Fetter,[1,2] Duncan A. Nowicki,[1,3] Iain R. Gibson[1] and Jan Skakle[1]

[1] University of Aberdeen, Scotland UK AB24 3UE
[2] Leibniz Universität Hannover, Welfengarten 1, D-30167 Hannover, Germany
[3]University of St. Andrews, North Haugh, St. Andrews, Scotland UK KY16 9ST

Previously, we have shown that hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) materials can accommodate large amounts of carbonate on both the OH (A) site and on the phosphate (B) site[1-4]. This gives it potential to act as a carbon capture material, with the added attraction that it (a) is cheap and relatively easy to synthesise at large scale and (b) has potential to be used as a fertiliser[5-6], thus fulfilling requirements for carbon-capture and usage (CCU). By substituting sodium at the calcium site, it is possible to incorporate more carbonate, but this is normally done by doping with sodium carbonates, rather than incorporating all carbonate from the air. Our previous utilised NaCl as a source of sodium ions combined with CO_2 gas dissolved in the reaction mixture[1].

In this study, we investigate the potential of using sea water as a source of sodium and supplying the carbonate both at high temperatures and through carbonated water. Samples were synthesised by an aqueous route, adding a solution H_3PO_4 to a suspension of $Ca(OH)_2$ and NaCl drop-wise, whilst stirring and maintaining pH at a value above 11. CO_2 was added to the water in the solutions by bubbling gas through the water prior to use, and in some cases into the H_3PO_4 solution during the synthesis. After synthesis, samples were heated under CO_2 gas at either 500°C or 1000°C; the former encourages B-site carbonate substitution, the latter A-site substitution.

Samples were analysed using powder XRD, FTIR, TG-MS, EDX and combustion synthesis. As with earlier studies using sodium carbonate as a source, much less sodium enters the structure than the designed composition. However, using carbonate bubbled into the H_3PO_4 solution during synthesis shows increased carbonate in the final product.

Overall, the results indicated that using NaCl resulted in less carbonate within the structure than for sodium carbonate co-substituted apatites, which might be expected; however, the carbonate that is included is directly obtained from gas, and thus a cost-benefit analysis may reveal that this is a more effective way to remove carbonate directly from a hot gas source.

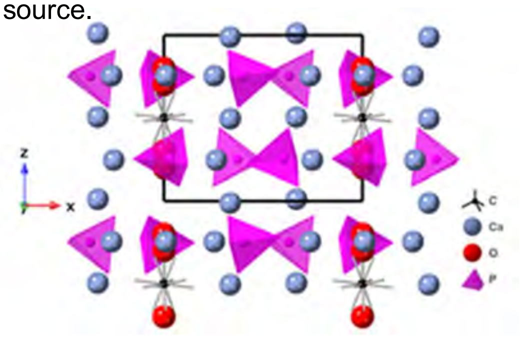


Figure: The crystal structure of carbonated hydroxyapatite, showing disordered A-site substitution

[1] D.A. Nowicki, J. M. S. Skakle, I.R. Gibson, *J. Mat. Chem. A*, 2018, **6(13)**,5367-5377.
[2] J. A. Stephen, C. Pace, J. M. S. Skakle, I. R. Gibson, *Key Eng Mat,* 2007, **330-332(I)**,19-22.
[3] J. Whyte, D. Hadden, I. R. Gibson, J. M. S. Skakle, *Key Eng. Mat.,* 2008;**361,** 207-210.
[4] D. A. Nowicki, J. M. S. Skakle, I. R. Gibson, *J. Solid State Chem,* 2021, **297**, 122042.
[5] R. Liu, L. Rattan, *Scientific Reports,* 2014, **4**, 5686.
[6] L. Xiong, P. Wang, M. N. Hunter, P. M. Kopittke, *Env. Sci: Nano*, 2018, **5(12),** 2888-2898.

Understanding the effect of lattice polarisability on the electrochemical properties of mechanochemically-synthesised lithium tetrahaloaluminates $LiAlX_4$ (X = Cl, Br, I)

N. Flores-González[1], N. Minafra[2], M. López[3], G. Dewald[4], H. Reardon[1], J. Bohnenberger[5],
R.I. Smith[6], P.J. Baker[6], S. Rudić[6], S. Adams[7], F. Viñes[3], I. Krossing[5], W.G. Zeier[2], F. Illas[3] and D. H. Gregory[1]
[1]WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ,
[2]Institute for Inorganic and Analytical Chemistry, University of Münster, 48149 Münster
[3]Institute of Theoretical and Computational Chemistry, University of Barcelona, 08028 Barcelona
[4]Institute of Physical Chemistry, Justus-Liebig-University Giessen, D-35392 Giessen
[5]Institut für Anorganische und Analytische Chemie, Freiburger Materialforschungszentrum (FMF)
Universität Freiburg, Albertstr. 21, 79104 Freiburg.
[6]ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX.
[7]Department of Materials Science and Engineering, National University of Singapore, 117575, Singapore.

Establishing links between the structure and physical properties of solid-state ionic conductors contributes not only to a rationale of their fundamental nature, but also provides design principles to accelerate the discovery of new materials. Lithium-ion conduction in complex halides is not well-elucidated and so the interplay between lattice dynamics, electronic structure, and electrochemical properties in such halides has been explored in the isostructural family of lithium tetrahaloaluminates $LiAlX_4$ (X = Cl, Br, I). In this work, we first show how high-purity $LiAlX_4$ powders can be easily synthesised by mechanochemical methods, which has enabled the synthesis of $LiAlI_4$ for the first time (Monoclinic $P2_1/c$, Z = 4; a = 8.0846(1) Å; b = 7.4369(1) Å; c = 14.8890(2) Å; β = 93.0457(8) °).[1] Of the tetrahaloaluminates, $LiAlBr_4$ exhibited the highest ionic conductivity at room temperature (0.033 mS cm^{-1}), while $LiAlCl_4$ showed a conductivity of 0.17 mS cm^{-1} at 333 K, coupled with the highest thermal and oxidative stability. Bond-valence site energy analyses (BVSE) show that the conduction mechanisms in the haloaluminates do not change significantly as a function of X, and that the lithium diffusion is dominated by 2D jumps along the *bc* plane. In particular, for $LiAlCl_4$, empirical molecular dynamics simulations shows that the 2D Li^+ motion in the *bc* plane is coupled to dynamic anion disorder. Using a combination of experimental methods (diffuse reflectance UV-Vis spectroscopy, pulse-echo speed of sound measurements, Raman spectroscopy, inelastic neutron scattering, muon-spin spectroscopy) and periodic Density Functional Theory (DFT) based calculations, we demonstrate that softer lattices (quantified in terms of Debye frequencies or Li-phonon band centres as a function of X) provide lower activation energies for Li^+ migration. However, the relationship between polarisability and Li^+ conductivity is not straightforward. In line with expectations emergent from the Meyer–Neldel rule, the activation energy for Li^+ hopping, E_a, and the pre-exponential terms collated as σ_0 in the Arrhenius equation for activated conductivity, correlate. It is also evident that the electrochemical oxidative potential limit correlates with the X^- phonon band centre in the Vibrational Density of States (VDOS) and that the Electrochemical stability Window (EW) and optical band gap are interlinked, as expected.[2]

1. N. Flores-González, N. Minafra, G. Dewald, H. Reardon, R. I. Smith, S. Adams, W. G. Zeier and D. H. Gregory, *ACS Mater. Letters*, 2021, **3**, 652-657.
2. N. Flores-González, M. López, N. Minafra, J. Bohnenberger, F. Viñes, S. Rudić, I. Krossing, W. G. Zeier, F. Illas and D. H. Gregory, *J. Mater. Chem. A*, 2022, **10**, 13467-13475.

Investigations into Columbites as Electrode Materials for Energy Storage Devices

Matthew Friskey[1], Xin Chen[1] and Julia Payne[1]

[1] School of Chemistry, Purdie Building, University of St Andrews, St Andrews, Scotland.

Three requirements of new energy storage devices are high energy density, high power density and high cyclability. As a result, new materials must bridge the gap between materials which can store a large amount of energy but are slower to charge (batteries), and materials which can charge extremely quickly with a limited energy density (supercapacitors). Columbites have shown a potential for high power and energy density as well as stability over many cycles but suffer from low conductivity, degradation, and irreversible metal ion loss.[1] Materials of the columbite structure show partial pseudocapacitive charge storage which combined with small volume changes during charging, low toxicity and high theoretical specific capacity make them well suited as negative electrode materials in high-rate Li-ion batteries.[2]

$M\text{Nb}_2\text{O}_6$ (M = Cu, Zn, Fe, Mn), have been studied in recent years for their use as negative electrode materials. Lee *et al.* fabricated $M\text{Nb}_2\text{O}_6$ (M = Cu, Zn, Mn) *via* a hydrothermal route and found CuNb_2O_6 could produce a high energy density but lacked the cycling stability of MnNb_2O_6.[2] Garcia-Alvarado *et al.* noted higher conductivity in $\text{MnNb}_2\text{O}_{6-\delta}$.[3] A hybrid FeNb_2O_6/reduced graphene oxide material produced by Kong *et al*. *via* a two-step hydrothermal synthesis was shown to provide a high energy density at different charging rates.[4]

MnNb_2O_6 has an orthorhombic unit cell, consisting of chains of corner-sharing MnO6 and NbO6 octahedra along the *a* axis.[3] In this work, we synthesise$\text{Mn}_{1-x}\text{Co}_x\text{Nb}_2\text{O}_6$ and study how this influences the crystal structure and electrochemical performance. Pouch cells have also been constructed for use in on-going *operando* XAS experiments to track changes in the oxidation states of the metal ions during the charge/discharge process.

References

[1] Y. Lian, Y. Zheng, D. Wang, Y. Bai, H. Yan, Z. Wang, J. Zhao, and H. Zhang, *J. Colloid Interface Sci.,* 2022, **606**, 77-86

[2] S. Lee, A. Lim, Y. Kwon, K. Cho and S. Yoon, *Inorg. Chem. Front.*, 2020, **7**, 3176

[3] F. Garcia-Alvarado, A. Orera, J. Canales-Vázquez, and J. T. S. Irvine, *Chem. Mater.,* 2006, **18**, 3827-3834

[4] S. Kong, X. Zhang, B. Jin, X. Guo, G. Zhang, H. Huang, X. Xiang, and K. Cheng, *RSC Adv.*, 2021, **11**, 32248

Investigating the Effects of Doping Layered $LiNiO_2$ Cathodes

Lavan Ganeshkumar,[1,2,3] Alex Squires[1,2,3] and David O. Scanlon[1,2,3].

[1] University College London, London, United Kingdom,

[2]The Faraday Institution, Quad One, Harwell Science and Innovation Campus,
Didcot OX11 0RA, United Kingdom,

[3]Thomas Young Centre, University College London, Gower Street, London WC1E
6BT, United Kingdom.

Lithium-ion batteries have long been established as the leading technology for energy storage devices due to their high energy density and longevity [1]. Common cathode materials for these batteries are layered oxides. $LiCoO_2$ (LCO) is a popular layered oxide which is commonly used within the electronic industry. Yet, socioeconomic issues has led to a push for Co-free cathode materials, especially for the automotive application [2]. The isostructural compound $LiNiO_2$ (LNO) is well placed as a replacement for LCO as it has theoretical capacity and voltages comparable to LCO[1]. However, the material cannot fully utilise its theoretical energy density due to its notorious mechanical and thermodynamical instabilities.

Recent work has demonstrated that substitution strategies can cater for the instabilities whilst minimising the reduction in capacity during cycling. Density functional theory (DFT) calculation, with its ability to predict the ground state structures and charge compensation mechanisms, have been an effective tool for investigating solid-state materials with dopants such as these. In this study, we implement DFT in order to fully understand the doped structure with the aim to find a stable Ni-rich cathode with a high theoretical capacity. As such, the intrinsic point defects are investigated in these cathode materials which reveal insight into experimental observations for LNO and provide an understanding for the charge compensating mechanisms within the pristine system. In addition, the study explores the effects of incorporating Mg and W as co-dopants within the pristine system. These dopants were selected based on their notable success as individual dopants reported in previous experimental studies[3,4].

[1] M. W. Chase Jr and N.-J. T. Tables, J. Phys. Chem. Ref. Data, Monograph, 1998, **9**, 1-1951.

[2] K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough, Mater. Res. Bull. 1980, **15**, 783–789.

[3] K. Hoang and M. D. Johannes, Journal of Materials Chemistry A, 2014, **2**, 5224–5235.

[4] H.-H. Ryu, G.-T. Park, C. S. Yoon and Y.-K. Sun, Journal of Materials Chemistry A, 2019, **7**, 18580–18588.

Mo_3Sb_7 and role of Te-doping on its electrocatalytic properties for water splitting reaction

Alexey Y. Ganin and James P. Fraser

School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, United Kingdom

Renewable energy sources will play a key role in the transition to a net zero emission economy. However, our ability to successfully manage the highs and lows in their supply and demand is currently very limited. The excess energy could be stored for later use as hydrogen harvested by splitting water into its constituent parts, in a device called electrolyser.[1] Proton exchange membrane (PEM) electrolysers are considered the best option for integration with renewable energy sources but they operate under acidic conditions.[2] This necessitates the use of Pt group metals as catalysts (of the hydrogen evolution reaction) as they can withstand the harsh operating conditions. The cost and scarcity associated with the Pt group metals creates the opportunities for research into finding earth-abundant, less expensive alternatives.[3]

Common binary materials have been extensively investigated, in this regard. However, one Mo-based compound has been overlooked for the use as a HER catalyst so far. Molybdenum antimonide, Mo_3Sb_7 has only attracted attention for its thermoelectric properties and potential application as an anode material for sodium- and lithium-ion batteries.[4,5] An interesting feature of this compound is the ability to replace up to 2 Sb atoms per formula unit with Te without changing the crystal structure of the parent compound. The $Mo_3Sb_{7-x}Te_x$ system, therefore, provides an interesting platform to study the influence of Te doping on catalytic activity without having to be concerned over structural changes.

In this work three solid-solutions of the cubic $Mo_3Sb_{7-x}Te_x$ (x = 0, 1, 1.6) series were synthesized, proved phase-pure by powder x-ray diffraction (PXRD) and probed by linear and cycling voltammetry as potential electrocatalysts. Mo_3Sb_7 showed a large overpotential of 570 mV at a current density of 10 mA cm^{-2}. However, the replacement of Sb with Te increased the stability of the catalyst and in the case of $Mo_3Sb_{5.4}Te_{1.6}$ reduced the overpotential required to achieve 10 mA cm^{-2} to 511 mV. This improvement in performance was also mirrored in the Tafel slopes of the materials with $Mo_3Sb_{5.4}Te_{1.6}$ having a Tafel slope of 136.2 ± 0.5 mV dec^{-1} compared to 167.5 ± 0.6 mV dec^{-1} exhibited by Mo_3Sb_7.

Although the three compounds tested are suboptimal HER catalysts, compared to other state-of-the-art materials, they nevertheless provide an interesting system to observe the effects of tellurium doping on the catalytic performance.

References

[1] S. Maddukuri, D. Malka, M. S. Chae, Y. Elias, S. Luski, D. Aurbach, *Electrochim Acta* 2020, **354**, 136771.

[2] S. Shiva Kumar, V. Himabindu, *Mater Sci Energy Technol* 2019, **2(3)**, 442.

[3] A. Y. Ganin, M. D. Symes, *Curr Opin Electrochem* 2022, **34**, 101001.

[4] E. Dashjav, A. Szczepenowska, H. Kleinke, *J Mater Chem* 2002, **12(2)**, 345.

[5] L. Baggetto, E. Allcorn, R. R. Unocic, A. Manthiram, G. M. Veith *J Mater Chem A Mater* 2013, **1(37)**, 11163.

Single crystal growth and properties of the polar metallic ferromagnet Mn$_{1.05}$Bi with Kagome layers, huge magnetic anisotropy and slow spin dynamics

Quinn D.Gibson,[1]Craig .M. Robertson[1], Matthew .S. Dyer[1], Marco Zanella[1], T. Wesley Surta[1], Luke M. Daniels[1], John B. Claridge[1], Jonathan Alaria[2], Matthew J. Rosseinsky[1]

[1] University of Liverpool Department of Chemistry, Crown Street, Liverpool, L69 7ZD, United Kingdom
[2] University of Liverpool Department of Physics, Oliver Lodge Laboratory, Liverpool, L69 7ZE, United Kingdom

The synthesis, structure and properties of single crystalline metastable Mn$_{1.05}$Bi in the polar space group Fdd2 are reported. Mn$_{1.05}$Bi is isostructural to the previously reported Mn$_{1.05}$Rh$_{0.02}$Bi[1], with both ordered interstitials and ordered vacancies of Mn leading to Kagome-like layers. The ordering of the interstitials breaks inversion symmetry and forces the material into a polar space group. DC magnetisation reveals ferromagnetic properties with a huge magnetic anisotropy, with the magnetisation pinned along the *a*-axis (the stacking axis), and multiple magnetic transitions which retain this anisotropy. AC measurements confirm these transitions and show very sluggish spin dynamics along the *a*-axis, with a very large temperature dependent out-of-phase response. Heat capacity measurements reveal the presence of Schottky defects, and resistivity measurement confirms the transitions and reveal the material to be dominated by magnetic scattering. Overall, Mn$_{1.05}$Bi shows magnetic properties markedly different from hexagonal, NiAs-type MnBi, driven by ordered interstitials and vacancies of Mn, stabilising a likely complex magnetic structure with strongly temperature dependent spin dynamics. This is supported by Density Functional Theory calculations, which suggest a strongly anisotropic non-collinear ground state driven by Kagome layers and asymmetric Mn environments. This demonstrates that careful control of defects in NiAs type materials can stabilise complex crystal structures with non-collinear magnetic ground states.

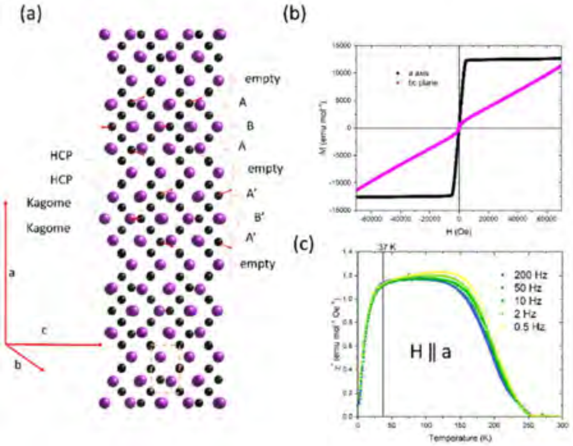


Figure 1. (a) Crystal structure of Fdd2 Mn$_{1.05}$Bi, showing both the defect ordering in the NiAs type layers and interstitial layers. Red arrows show the displacement direction of the interstitial Mn. (b) Magnetisation versus field curves for the field applied along *a* and in the *bc* plane, showing incredibly anisotropic ferromagnetism. (c) Out-of-phase AC susceptibility, showing a large response indicating very sluggish spin dynamics.

[1] V. Taufour, S. Thimmaiah, S. March, S. Saunders, K. Sun, T. N. Lamichhane, M. J. Kramer, S. L. Bud'ko, and P. C. Canfield, *Phys. Rev. Appl*. 2015, **4**, 014021.

Anion Redox as a Means to Derive Layered Manganese Oxychalcogenides with Exotic Intergrowth Structure

Souvik Giri,[1] Shunsuke Sasaki[1], Simon Cassidy[1], Sunita Dey[2], Giannantonio Cibin[3], Clare Grey[2] and Simon Clarke[1]

[1] Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

[2] Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK

[3] Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK.

Topochemistry enables step-by-step conversions of solid-state materials often leading to metastable structures that retain initial structural motifs. Recent advances in this field revealed many examples where relatively bulky anionic constituents were actively involved in redox reactions during (de)intercalation processes. Such reactions are often accompanied by anion-anion bond formation, which heralds possibilities to design novel structure types disparate from known precursors, in a controlled manner. Here multistep conversion is presented of layered oxychalcogenides $Sr_2MnO_2Cu_{1.5}Se_2$ into Cu-deintercalated phase where antifluorite type $(Cu_{1.5}Se_2)^{2.5-}$ slabs collapsed into 2D arrays of chalcogen dimers. The collapse of the selenide layers on deintercalation led to various stacking types of $Sr_2MnO_2Se_2$ slabs, which formed unprecedented polychalcogenide structures unattainable by conventional high-temperature syntheses. We understand the structure using X-ray diffraction and spectroscopy along with various other techniques. Anion-redox topochemistry is demonstrated to be of interest not only for electrochemical applications but also to design of complex novel layered architectures.

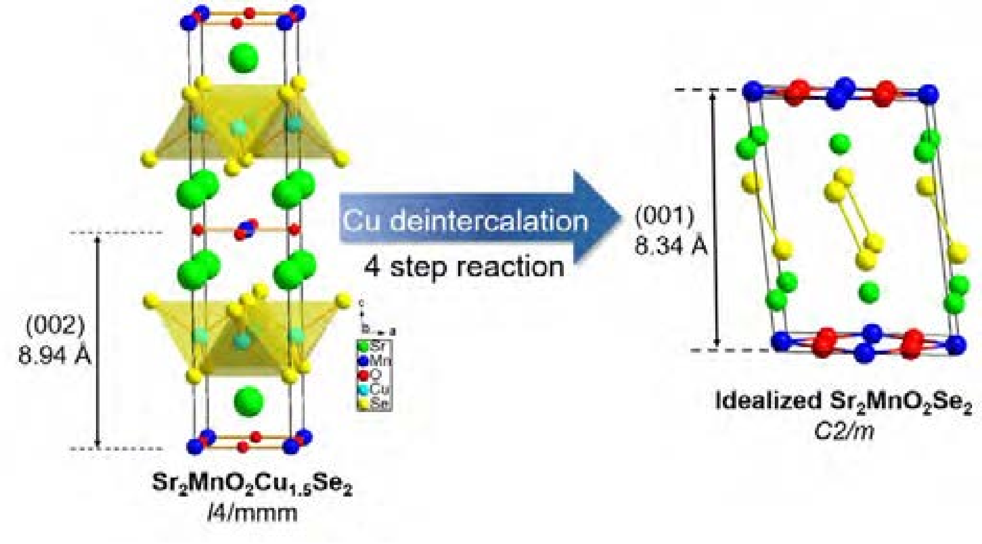


Fig 1: Multistep oxidative Cu deintercalation leads to collapse of CuCh layer forming 2D array of anion dimers

Co-Existing Long- and Short-Range Magnetic Order in the Frustrated Diamond Antiferromagnet, $LiYbO_2$

J. N. Graham[1,2], N. Qureshi[1], P. Manuel[3], C. Ritter[1], A. R. Wildes[1] and L. Clark[2]

[1] Institut Laue-Langevin, 71 avenue des Martyrs, 38000 Grenoble, France

[2] School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

[3] ISIS Facility, Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11, 0QX, UK

The field of frustrated magnetism explores the unconventional magnetic ground states that arise due to the competition of exchange interactions between magnetic moments [1]. Recently, a new frustrated magnet, LiYbO2, has attracted attention as it contains several complex magnetic phases within an unusual stretched diamond lattice [2-4]. We have prepared a polycrystalline sample, and collected high-resolution diffraction data on D2B, explored the long-range magnetic ordered states on WISH and short-range diffuse scattering on D7. Our results confirm an incommensurate helical ground state below 450 mK, with propagation vector, **k** = (0.391, ±0.391, 0), and $\mu_{eff} = 1.2\mu_B$. Crucially, we find that the phase angle between the two magnetic sublattices within the stretched diamond network is 1.1π, which makes $LiYbO_2$ the first experimental realisation of the spiral-spin liquid phase on an elongated diamond lattice. Additionally, between 450 mK and 1.13 K we propose a new intermediary magnetic ordered phase, where the propagation vector and moment size vary as a function of temperature. Surrounding the well-ordered magnetic Bragg peaks there is significant diffuse scattering. We have analysed these data with state-of-the-art SPINVERT RMC spin simulations which allowed us to explore the interplay between ordered and disordered correlations. Correlated magnetic disorder exists down to 50 mK indicating that a fraction of the sample remains frustrated and so $LiYbO_2$ has a partially disordered magnetic ground state.

References

[1] L. Clark and A. H. Abdeldaim, Ann. Rev. Mater. Res. **51**: 495-519 (2021)

[2] Y. Hashimoto *et al.* J. Phys. Condens. Matter **32** (2002)

[3] M. M. Bordelon *et al.* Phys. Rev. B. **103**, 014420 (2021)

[4] E. M. Kenney *et al.* arXiv:2205.00052 (2022)

Modelling the NMR spectra of solid solutions: DFT simulations and machine learning

Ricardo Grau-Crespo,[1] Said Hamad,[2] Salvador R. G. Balestra,[2] David McKay[3] and Sharon E. Ashbrook.[3]

[1] Department of Chemistry, University of Reading, UK,

[2] Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, Seville, Spain,

[3] School of Chemistry, University of St Andrews, UK.

The theory to obtain nuclear magnetic resonance (NMR) chemical shifts from quantum-mechanical simulations in a periodic solid is well established,[1] but the difficulty in applying such techniques to solid solutions lies in the statistical treatment of site disorder. We recently developed an approach for the statistical modelling of the NMR spectra of solid solutions.[2] In that work, chemical shifts were calculated for all configurations in a symmetry-adapted canonical ensemble and combined to form the solid solution spectrum, providing reasonable agreement with experiment. However, that methodology had some important limitations: a) the variety of local chemical environments that can be achieved in a canonical ensemble is incomplete, and b) the computational cost of calculating chemical shifts for all configurations in a large ensemble is huge. We have now developed a much-improved strategy, which will be presented in this talk. First, a grand-canonical ensemble, where we can mix supercell configurations with different compositions, can achieve all the possible local chemical environments. Second, we show how ensemble truncation and machine-learning tools can be used to alleviate the computational cost of our simulations. We demonstrate the effectiveness of our methodology using the pyrochlore solid solution $La_2(Zr,Sn)_2O_7$, for which our simulations give a level of agreement with experiment that could not be obtained with previous approaches (Figure 1). We also discuss how our new approach, which is implemented in the SOD (Site Occupancy Disorder) package,[3] can be more generally useful in the computer simulation of solid solutions, for example by providing a better description of the thermodynamics of mixing of the solid solution, or by allowing the consideration of equilibrium with external phases.

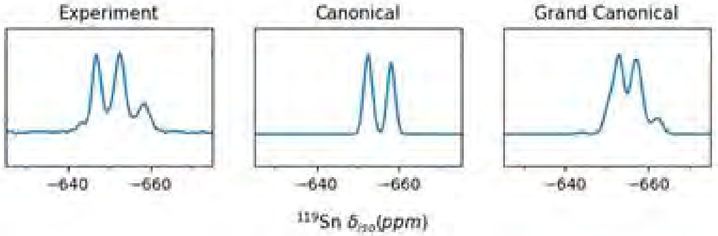


Figure 1: Comparison of the experimental ^{119}Sn NMR spectrum of $La_2(Sn_{0.125}Zr_{0.875})_2O_7$ with those obtained using DFT simulations in combination with canonical or grand canonical statistical mechanics.

References

[1] C.J. Pickard and F. Mauri, *Phys. Rev. B*, 2001, **63**, 245101.

[2] R.F. Moran, D. McKay, P.C. Tornstrom, A. Aziz, A. Fernandes, R. Grau-Crespo, S. E. Ashbrook. *J. Am. Chem. Soc.*, 2019, **141**, 17838–17846.

[3] Site Occupancy Disorder (SOD) code. https://github.com/gcmt-group/sod.

Alkali-rich Oxide Perovskites - A Solid-State Chemist's Playground for Exploring Structure-Property Relationships for Battery Applications

Peter Gross,[1] Professor Serena Cussen[1] and Professor Eddie Cussen. [1]

[1] University of Sheffield, Department of Materials Science and Engineering.

A key challenge in the ongoing energy transition persists in finding affordable, long-lived and safe electrochemical storage devices for grid stabilisation. Our long-term vision to overcome this crucial issue are all-ceramic pseudo-monophasic sodium ion batteries. In order to realise such a holistic approach, we explore the novel class of alkali-rich perovskite materials.[1-3] These materials offer the unique opportunity to simultaneously tailor their electrical and ionic conductivity as well as electrochemical activity, while still adopting the same crystal structure type. With the series $Na_{1.5}La_{1.5}Te_{1-x}W_xO_6$ we present the first example of a sodium-ion battery material that can be tuned by chemical substitution to work either as solid electrolyte ($x = 0$) or as active material ($x = 0.9$). Synthesis as well as the characterisation of structural, electrochemical and transport properties are presented. Furthermore, we present with the new compound family $Na_{1.5}Ln_{1.5}TeO_6$ (*Ln* = La-Lu, except Ce, Pm) a unique playground to selectively synthesise materials in one of three different structure types, solely dependent on the ionic radius of the lanthanide ion. While early lanthanides (*Ln* = La-Nd) adopt a double perovskite featuring a disordered A site (75% *Ln*, 25% Na) and Na and Te on rock-salt ordered B sites (Fig. 1a), intermediate lanthanides (*Ln* = Sm-Ho) show additional layered A-site ordering and superstructure reflections (Fig. 1b), and late lanthanides (*Ln* = Ho-Lu) crystallise as single perovskites in the $GdFeO_3$ type, featuring mixed occupation on both A (75% Na, 25% *Ln*) and B (50% *Ln*, 50% Te) sites (Fig. 1c). We show that the Goldschmidt tolerance factor[4] is a valuable tool for reliable prediction of stable perovskite lattice formation within this system. Finally, we discuss with $(Li_{0.25}Na_{0.75})_{1.5}Ln_{1.5}TeO_6$ (*Ln* = Pr-Gd) a serendipitously encountered, new 8H hexagonal perovskite,[5] which might offer new means to influence electrochemistry and transport properties for future materials.

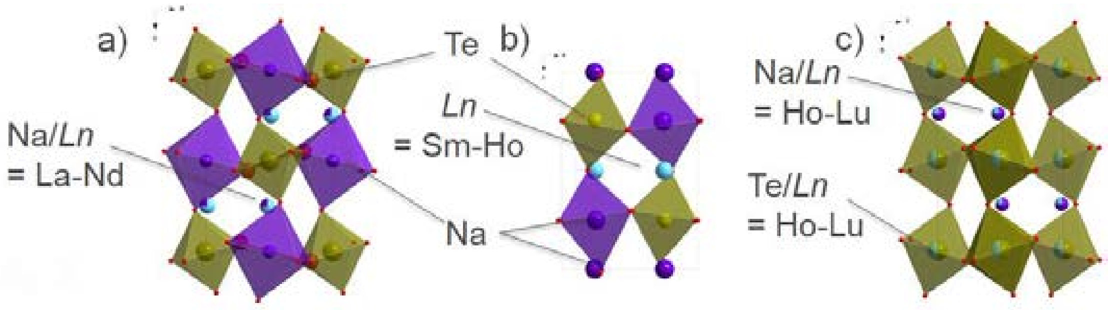


Fig 1. Crystal structures formed by early (*Ln* = La-Nd), intermediate (*Ln* = Sm-Ho) and late (*Ln* = Ho-Lu) lanthanide ions in the system $Na_{1.5}Ln_{1.5}TeO_6$.

References

[1] A. B. Santibáñez-Mendieta et al., *Chem. Mater.*, 2016, **28**, 7833-7851.
[2] M. Amores et al., *Chem. Commun.,* 2018, **54**, 10040.
[3] M. Amores et al., *Nature Commun.,* 2020, **11** 6392.
[4] V. Goldschmidt, *Naturwissenschaften,* 1926, **21**, 477-485.
[5] A. J. Jacobson et al., *Acta Cryst. B***,** 1974, **30**, 1705-1711.

Chemically inspired high throughput study for new stable ferroelectric nitride perovskites

Bastien F. Grosso,[1] Daniel W. Davies,[1] Bonan Zhu,[1] Aron Walsh [2] and David O. Scanlon[1]

[1]*Department of Chemistry, University College London, London, United Kingdom*

[2]*Department of Materials, Imperial College London, London, United Kingdom*

Nitride perovskites, with ABN_3 formula, have the potential to start a new paradigm in semiconductor devices. Indeed, this new class of materials is of great interest for developing oxygen-free functional materials, integrable in microelectronic devices and able to operate at low voltage. In this talk, we present a high throughput study of (AB)-N_3 compositional space and show how candidate materials can be identified using simple chemical and structural considerations. We further thoroughly explore the potential energy surface of our candidate materials using symmetry elements and ab initio random structure searching (AIRSS) in order to identify a possible ground state structure. The outcome of our workflow is twofold. On the one hand, we provide new insights on the ground state structure of already identified candidate compositions and on the other hand we propose new thermodynamically stable, likely synthesizable, nitride perovskites. We conclude our study by highlighting the interesting functionalities of our most promising candidates and in particular we evaluate their potential for being ferroelectric.

XPS Investigation of New Oxyfluoride Spinel Li Cathode with Redox-Active Ni and Mn

Hong Cai,[1] Ruiyong Chen,[1] Mounib Bahri,[2] Cara J. Hawkins,[1] Manel Sonni,[1] Luke M. Daniels,[1] Jungwoo Lim,[1,3] Jae Evans,[1] Marco Zanella,[1] Leanne A. H. Jones,[3] Troy D. Manning,[1] Tim D. Veal,[3] Laurence J. Hardwick,[1,3] Matthew S. Dyer,[1] Nigel D. Browning,[2] John B. Claridge,[1] Matthew J. Rosseinsky[1]

[1] Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD,
Liverpool, United Kingdom
[2] Albert Crewe Centre, University of Liverpool, Research Technology Building,
Elisabeth Street, Pembroke Place, L69 3GE, Liverpool, United Kingdom
[3] Stephenson Institute for Renewable Energy, University of Liverpool, Peach Street,
L69 7ZF, Liverpool, United Kingdom

The discovery of new cathode materials with improved energy densities and cyclability continues the advancement of Li ion batteries (LIBs) for applications in Electric Vehicles (EV), among others. Spinel materials (e.g $LiMn_2O_4$) have become established cathode materials owing to fast Li transport through the material. However, Mn-based cathodes suffer from irreversible phase transitions[1], instability at elevated temperatures[2] and dissolution into the liquid electrolyte[3]. Accessing higher cell potential can be achieved through inclusion of Ni in the spinel structure (e.g. $LiNi_{0.5}Mn_{1.5}O_4$) though these materials suffer from capacity fade at elevated temperatures[4, 5]. Understanding fundamental ion intercalation mechanisms through *in situ* and *ex situ* characterisation of cathode materials is key to improving capacity losses.

Here, a new Li-Ni-Mn-O-F spinel with significant cation disorder is reported and characterised through combined refinement of X-ray and neutron diffraction data. This material demonstrates capacities of 225 mAh g^{-1} at 25 °C, far exceeding $LiNi_{0.5}Mn_{1.5}O_4$. X-ray Photoelectron Spectroscopy (XPS) is used to understand the involvement of Ni/Mn redox upon cycling to high (5 and 5.3 V) and low (2 and 1.5 V) potentials. Both Ni and Mn are redox-active, and reversible Li^+ intercalation is observed in XPS of the Li 1s core level.

This spinel exhibits improved cyclability, owing to high structural integrity over cycling, and increased capacity, arising from additional Li^+ intercalation as well as Mn^{4+}/Mn^{3+} redox mechanisms confirmed by XPS. The involvement of Mn redox in this spinel contrasts with $LiNi_{0.5}Mn_{1.5}O_4$, where Mn^{4+} remains unchanged and only Ni^{4+}/Ni^{2+} redox is observed[4, 5]. Hence, it is shown that Mn redox is responsible for the enhanced electrochemical performance over end-member $LiNi_{0.5}Mn_{1.5}O_4$, and is accessed through incorporation of fluoride.

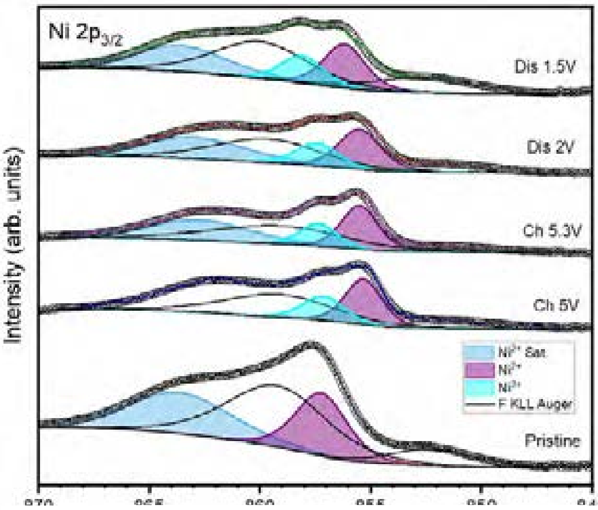


Figure 5 - Ex situ *XPS spectra of Ni $2p_{3/2}$ core level for samples of Li-Ni-Mn-O-F powder at different stages of charge (5 and 5.3 V) and discharge (2 and 1.5 V) as well as the pristine material.*

[1] Manthiram, A.; *Nat Commun*. 2020, **11**, 1550.
[2] Lu, D., Xu, M., Zhou, L. et al.; *J. Electrochem. Soc*. 2013, **160**, A3138-A3143.
[3] Zhou, G., Sun, H., Li, Q-H. et al.; *J. Phys. Chem. Lett*. 2020 **11** (8), 3051-3057
[4] Manthiram, A., Chemelewski, K., Lee, E-S.; et al. *Energy Environ. Sci*. 2014, **7**, 1339-1350.
[5] Liu, D.; Zhu, W., Trottier, J. et al. *RSC Adv*. 2014, **4**, 154-167.

Understanding the Local Structure of Protective Alumina Coatings for Cathodes and the Coating-Cathode Interface

Abby R. Haworth,[1,5] Beth I. J. Johnston,[2,5] Laura Wheatcroft,[3,5] Samuel G. Booth,[2,5]
Alisyn J. Nedoma,[2,5] Serena A. Cussen,[3,5] and John M. Griffin[1,4,5]

[1]Department of Chemistry, Lancaster University, Lancaster, LA1 4YB, UK
[2]Department of Chemical and Biological Engineering, University of Sheffield, Sheffield, S1 3JD, UK
[3]Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, UK
[4]Materials Science Institute, Lancaster University, Lancaster, LA1 4YB, UK
[5]The Faraday Institution, Quad One, Harwell Campus, OX11 0RA, UK

Batteries are becoming increasingly popular and are set to play an important role in the transition towards a net-zero carbon economy. In particular, lithium-ion batteries have gained considerable interest as a result of their use in portable electronic devices, as well as growing applications for electric and hybrid vehicles. However, they still face a number of challenges that need to be overcome. One such challenge is the capacity fade which arises over multiple charge-discharge cycles as a result of unwanted reactions at the electrode-electrolyte interface.

This project focuses on tailoring protective coatings to help improve cathode longevity and ultimately battery lifetime. Thin Al_2O_3 coatings have been demonstrated to extend the cycle life for various cathode materials, including $LiCoO_2$ (LCO) and $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC).[1,2] Our studies, within the Faraday Institution-funded FutureCat project focus, on lithium nickel oxide ($LiNiO_2$ – LNO). This is a cobalt-free alternative to the commonly used cathode materials, LCO and NMC. Although it has the potential to be used as a cathode material in next-generation electric vehicles, it suffers from capacity fade over multiple cycles.[3] Al_2O_3 coatings are being developed within the FutureCat consortium to mitigate side reactions causing capacity loss for LNO cathodes. However, the structure of Al_2O_3 within these coatings and how it interfaces with LNO are not well understood. In order to improve and tailor coatings for cathode materials, it is important to first fully understand the structure of the coating, any reactions occurring at the coating-cathode interface, and the ion dynamics at the coating-cathode interface.

To probe this further, Al_2O_3 coatings have been studied using solid-state NMR spectroscopy. The latest ^{27}Al MAS NMR data, which will be presented here, suggests that additional phases are present alongside the Al_2O_3 coating. These are believed to be the result of aluminium/lithium mixing occurring at the coating-cathode interface during the coating procedure. This is valuable insight into the structure of both these coatings and the coating-cathode interface. This additional structural insight, in conjunction with ab-initio computation studies ongoing within the FutureCat consortium, will enable the ion transport across the interface and through the coating to be understood in greater detail.

References

[1] S-T. Myung, *et al. Chem. Mater.* 2005, **17**, 3695-3704.
[2] A. M. Kannan, *et al. Electrochem. Solid-State Lett.* 2003, **6**, A16-A18.
[3] M. Bianchini*, et al. Angew. Chem. Int. Ed.* 2019, **58**, 10434-10458.

Exploring Stability & Synthesis of Quaternary Oxysulfides for Visible-Light Photocatalysis

Glen R. Hebberd,[1] Emma E. McCabe,[1] Stewart Clark,[1] and Matthew Dyer.[2]

[1] Department of Physics, Durham University, Lower Mountjoy, South Road, Durham, DH1 3LE.

[2] Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD.

Photocatalysts for water splitting that are active under visible light have the potential to provide a sustainable supply of hydrogen for energy generation and storage. Many oxide photocatalysts have band gaps too large for the visible light region of the solar spectrum. Replacing some oxide anions with sulfide anions, forming oxysulfides, can decrease the bandgap towards the visible region.[1] In addition to the band gap and band edge positions, other design features may enhance electron-hole separation and photocatalytic performance, including the cation electron configuration, polar coordination environments and a polar crystal structure.[2] The structural chemistry of oxysulfides, in terms of dimensionality and homoleptic vs heteroleptic coordination environments is not yet fully understood[3] but is thought to be critical to optimising photocatalytic activity.[4]

Our research focuses on quaternary oxysulfides. We combine experiment and theory to design and prepare new phases, and to investigate the roles polarity and connectivity, coordination environment and cation electron configuration. We present here work on $La_2O_2MS_2$-related materials (Figure 1).

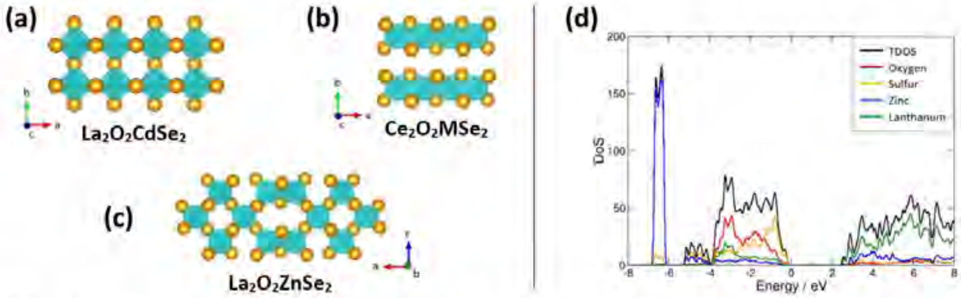


Figure 1 Panels (a) – (c) show crystal structures of several $La_2O_2MS_2$-related phases (M = divalent transition metal or *p*-block cation) and (d) shows total (TDOS) and partial density of states of predicted $La_2O_2ZnS_2$ (isostructural to corresponding oxyselenide).

Density functional theory calculations have been used to investigate the electronic structure of synthetic targets and formation energy calculations have helped choose between synthesis routes including traditional high-temperature solid-state reactions, ball-milling methods and topotactic reactions.[5,6]

References

[1] K. Chatterjee and S. E. Skrabalak, *ACS Appl. Mater. Interfaces*, 2021, **13**, 36670-36678.

[2] S. Al Bacha, S. Saitzek, E. E. McCabe and H. Kabbour, *Inorg. Chem.*, 2022, DOI: 10.1021/acs.inorgchem.2c03040.

[3] M. Orr, G. R. Hebberd, E. E. McCabe and R. T. Macaluso, *ACS Omega*, 2022, **7**, 8209-8218.

[4] N. Vonrüti and U. Aschauer, *J. Mater. Chem. A*, 2019, **7**, 15741-15748.

[5] S. Sasaki, D. Driss, E. Grange, J.-Y. Mevellec, M. T. Caldes, C. Guillot-Deudon, S. Cadars, B. Corraze, E. Janod, S. Jobic and L. Cario, *Angew. Chem. Int. Ed.*, 2018, **57**, 13618-13623.

[6] J. Gamon, A. J. Perez, L. A. H. Jones, M. Zanella, L. M. Daniels, R. E. Morris, C. C. Tang, T. D. Veal, L. J. Hardwick, M. S. Dyer, J. B. Claridge and M. J. Rosseinsky, *J. Mater. Chem. A*, 2020, **8**, 20553-20569.

$Sr_2Sb_2O_7$ as a novel thermoelectric material

Luisa Herring Rodriguez[a], David O. Scanlon[a,b]

[a] Department of Chemistry, University College London, 20 Gordon Street, London
WC1H 0AJ, United Kingdom

[b]Thomas Young Centre, University College London, Gower Street, London WC1E
6BT, United Kingdom

Around 60% of primary energy consumption is wasted as heat energy, representing an untapped source of energy with huge potential to reduce our overall consumption.[1] Thermoelectric materials convert heat energy into electricity through the use of temperature gradients. The materials historically used for this purpose include bismuth chalcogenides and lead tellurides. However, issues relating to their natural abundance and toxicity, combined with the increasing demand for environmentally friendly energy sources, is driving research into novel materials with potential thermoelectric properties to replace these.

The effectiveness of a thermoelectric is measured by the dimensionless figure of merit ZT. Materials with a high ZT need to balance a high electrical conductivity and a low thermal conductivity. Oxides generally exhibit properties valuable for thermoelectric applications, including low cost, thermal and chemical stability and environmental benignity. However, their thermoelectric performance has been hindered by their high lattice thermal conductivities. Novel ternary oxides have advanced research in this field as their complex crystal structures possess lower lattice thermal conductivities than traditionally seen in oxides.

In this study, we conduct a detailed investigation into the thermoelectric properties of the ternary wide band semiconductor $Sr_2Sb_2O_7$, which has previously been synthesised under high temperature conditions in previous studies and shown to be thermally stable.[2,3] Our study uses the latest approach to separately calculate the different contributions to overall scattering rates, in order to more accurately predict the transport properties[4]. We show that $Sr_2Sb_2O_7$ possesses a ZT greater than many existing oxide thermoelectric materials at a value of 0.71 and has the potential to perform as a high-performance n-type thermoelectric component. We go on to investigate the defect chemistry of this exciting new thermoelectric candidate to determine its doping capabilities and further assess its suitability.

References

[1] M Kanatzidis, Chem. Matter. 2010, 22, 648

[2] Sato et al., J. Photochem. Photobiol., A 2002, 148, 85

[3] Xue et al., J. Phys. Chem. C 2008, 112, 5850

[4] Ganose et al., Nat. Commun. 2021,12, 2222

Nickel (Hydroxy)Fluorides from Solution Chemistry

Craig I. Hiley, Richard I. Walton and Mark S. Senn

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK.

Although K_2NiF_4 is the archetypal Ruddlesden-Popper (n = 1) phase, transition metal fluoride perovskites and perovskite-related structures are far less studied than their oxide counterparts. A major reason for this is the difficulty in their preparation, which often utilises solid-state synthesis (where only the most thermodynamically stable phases can be accessed) or requires highly corrosive and/or toxic precursors, such as F_2 or HF. It was recently demonstrated that low-temperature solution methods without HF can yield $NaCrF_3$, containing Cr^{2+}.[1]

We are currently conducting an exploratory study of solution methods for the preparation of fluoride perovskite-related phases without the use of dangerous fluorinating agents. As part of this study we have discovered Ni(OH)F, a new hydroxyfluoride adopting the diaspore structure. Transition metal hydroxyfluorides have recently been explored for their magnetic properties.[2, 3]

$NaNiF_3 \cdot 3H_2O$, an ordered ReO_3-type phase[4] has also been prepared, and its transformation to orthorhombic perovskite (space group *Pbnm*) $NaNiF_3$ at ~150 °C has been explored.

Finally, $KNiF_3$ (space group $Pm\bar{3}m$) has been prepared by the hydrothermal reaction of KHF_2 and $NiCl_2 \cdot 6H_2O$ at 200 °C.

Powder X-ray diffraction and other characterisation data (including IR spectroscopy and magnetic susceptibility measurements) from these materials will be presented.

References

[1] Bernal, F. L. M.; Sottmann, J.; Wragg, D. S.; Fjellvåg, H.; Fjellvåg, Ø. S.; Drathen, C.; Sławiński, W. A.; Løvvik, O. M. *Phys. Rev. Mater.* 2020, **4**, 054412.

[2] Ben Yahia, H.; Shikano, M.; Tabuchi, M.; Kobayashi, H.; Avdeev, M.; Tan, T. T.; Liu, S.; Ling, C. D. *Inorg. Chem.* 2014, **53**, 365-374.

[3] Tustain, K.; McCabe, E. E.; Arevalo-Lopez, A. M.; Gibbs, A. S.; Thompson, S. P.; Murray, C. A.; Ritter, C.; Clark, L. *Chem. Mater.* 2021, **33**, 9638-9651.

[4] Gonzalo, E. C.; Sanjuán, M. L.; Hoelzel, M.; Azcondo, M. T.; Amador, U.; Sobrados, I.; Sanz, J.; García-Alvarado, F.; Kuhn, A. *Inorg. Chem.* 2015, **54**, 3172-3182.

Tunability of Zero-Dimensional Organic-Inorganic Metal Halides Utilizing the *m*-Xylylenediammonium Cation: MXDBiI$_{5\text{-}x}$Br$_x$ and MXDBiBr$_{5\text{-}y}$Cl$_y$

Yuri Hirano[1], Pia S. Klee[1], David B. Cordes[1], Alexandra M. Z. Slawin[1], and Julia L. Payne.[1]
[1] School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, UK, KY16 9ST

Photovoltaic devices based on $CH_3NH_3PbI_3$, an organic-inorganic lead halide perovskite, have seen power conversion efficiencies increase from 3.9 % to 25 % over the past decade.[1] This is astounding and suggests the potential of such materials to influence the next generation of photovoltaic devices. Research is underway in a variety of fields, from the development of new materials to the generation of films and the improvement of device efficiency. There is also a need to discover light-harvesting materials for commercialisation that are stable under ambient conditions and that do not use toxic lead. Here, organic-inorganic metal halides based on meta-xylylenediammonium (MXD) are reported.[2,3] MXD is an ammonium cation with an aromatic ring and is expected to improve moisture resistance.[4] The bismuth halide compounds, $MXDBiI_5$, $MXD_3Bi_2Br_{12}·2H_2O$ and $MXDBiCl_5$ were prepared using a solution-based method. The structure of three materials have been determined by single crystal X-ray diffraction and have zero-dimensional structures.

We explored the possibility of band gap engineering in these materials by preparing the mixed halides $MXDBiI_{5-x}Br_x$ ($0 < x < 3.71$) and $MXDBiBr_{5-y}Cl_y$ ($0 < y < 5.00$) by partial substitution of halides. A large range of solid solution was found for $MXDBiI_{5-x}Br_x$ and $MXDBiBr_{5-y}Cl_y$. Together, we found that the band gap of the MXD-based bismuth halide compounds can be tuned in the range 2.15 eV to 2.81 eV to 3.32 eV as we go from $MXDBiI_5$ to $MXD_3Bi_2Br_{12}·2H_2O$ to $MXDBiCl_5$ (Figure 1).

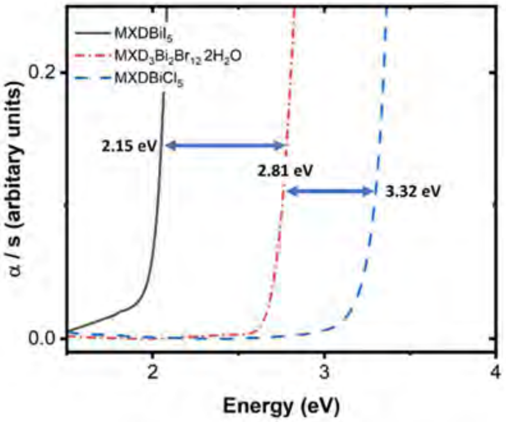


Figure1: UV-vis diffuse reflectance spectra of $MXDBiCl_5$, $MXDBiI_5$ and $MXD_3Bi_2Br_{12}·2H_2O$ converted using the Kubelka–Munk transformation ($\alpha/s = (1 - R)^2/2R$).

[References]
[1] *https://www.nrel.gov/pv/cell-efficiency.html* (Accessed: November 2022)
[2] P. S. Klee, Y. Hirano, D. B. Cordes, A. M. Z. Slawin and J. L. Payne., *Cryst. Growth. Des*. 2022, 22, 6, 3815–3823
[3] Y. Hirano and J. L. Payne, *in preparation*, 2022.
[4] I. Smith, E. Hoke, D. Solis-Ibarra, M. McGehee and H. Karunadasa, *Angew. Chem. Int. Ed.*, 2014, 53, 11232-11235

Dynamic disorder in layered covalent-organic frameworks

Ju Huang* **and Aron Walsh**

Thomas Young Centre and Department of Materials, Imperial College London, UK

Layered covalent organic frameworks (2D COFs) exhibit a high degree of structural flexibility and chemical stability, making them promising candidates in energy storage and conversion applications. However, their weak interlayer interactions mean stacking faults are common. These imperfections can significantly affect their performance in energy technologies arising from variations in crystallinity, porosity, and electrical conductivity. To date, many studies have reported ideal eclipsed stacking from powder X-ray diffraction (XRD) measurements, however, there is growing evidence that 2D COFs are disordered with offsets between layers.

Herein, we address this issue by studying the displacive instabilities in two prototypical COFs, Tp-Azo and DAAQ-TFP that have been used as high-performance Li ion battery electrodes. We demonstrate the existence of an unusual "sombrero" potential energy surface (PES) for layer displacements. The "sombrero" potential energy surface exhibits a striking preference for slipped structures with horizontal offsets between layers ranging from 1.7 Å to 3.5 Å in a potential energy minimum that forms a low energy ring. Furthermore, we elucidate the effects of interlayer π-π interactions on the electronic band structures and band gaps in eclipsed and slipped stacking sequences. We reveal a pronounced band gap opening of 0.8 - 1.4 eV in slipped arrangements that arises from subtle changes in the interlayer π orbital overlap. We further develop and apply machine-learned forcefields to efficiently model the COF dynamics over longer length and time scales.

Treatment of dynamic disorder is critical for screening COFs for applications in energy storage and conversion systems where electrochemical and photochemical descriptors are significantly altered including accessible voltage ranges for batteries, stability windows for electrocatalysis, and visible light absorption for photoelectrochemical systems.

This work was performed in collaboration with Matthias Golomb, Seán Kavanagh, Alex Ganose, Kasper Tolborg and Seung-Jae Shin. All calculations were run on the Archer2 supercomputer with access provided through the materials chemistry consortium.

References

[1] Huang, J., Golomb, M.J., Kavanagh, S.R., Tolborg, K., Ganose, A.M. and Walsh, A., 2022. Band gap opening from displacive instabilities in layered covalent-organic frameworks †. ***J. Mater. Chem. A**, 2022,**10**, 13500-13507*.

High conductivity in Na^+-ion conducting solid electrolytes for Na-ion batteries through a co-doping strategy

Xuankai Huang,[1] Haixue Yan[2] and Isaac Abrahams.[1]

[1]Department of Chemistry, Queen Mary University of London, Mile End Road
London, E1 4NS, U.K.

[2]School of Engineering and Materials Science, Queen Mary University of London,
Mile End Road London, E1 4NS, U.K.

Rechargeable batteries are regarded as the most promising energy storage technology because of their reliability and high energy conversion efficiency. Although Li-ion batteries (LIBs) have been widely used in portable electronic devices, Na-ion batteries (NIBs) are considered as a potential candidate to replace LIBs because of their non-toxicity, low cost, and elemental abundance. [1−6]

Solid state sodium-ion batteries are seen as potential cheaper and safer alternatives to current lithium-ion battery systems. The replacement of the presently used liquid electrolytes by non-flammable solid electrolytes is an important avenue to create safer batteries, while the high natural abundance of sodium compared to lithium would allow for significant cost reduction. The sodium superionic conductor, NASICON, first reported by Hong,[7] is one of the best-known sodium-ion conducting solid electrolytes, displaying high bulk ionic conductivity and good stability toward NASICON -based electrodes.[8,9] However, the practical use of NASICON has been impeded by low ion mobility at room temperature and poor interfacial connectivity. [10]

Here, the improvement of total conductivity has been achieved via La and Zn co-doping of NASICON. Total conductivity values of 4.68×10^{-3} S cm^{-1} at room temperature and 2.89×10^{-2} S cm^{-1} at 100 °C were obtained for $Na_{3.3}Zr_{1.8}La_{0.1}Zn_{0.1}Si_2PO_{12}$, which are amongst the highest values recorded for a NASICON based system. Furthermore, the system shows good air stability and could represent a suitable material for application in the field of Na-ion batteries.

References

[1] Kundu, D.; Talaie, E.; Duffort, V.; Nazar, L. F. Angew. Chem., Int. Ed. 2015, 54, 3431−3448.
[2] Hueso, K. B.; Armand, M.; Rojo, T. Sci. 2013, 6, 734−749.
[3] Kim, S.-W.; Seo, D.-H.; Ma, X.; Ceder, G.; Kang, K. Adv. Energy Mater. 2012, 2, 710−721.
[4] Palomares, V.; Serras, P.; Villaluenga, I.; Hueso, K. B.; CarreteroGonzález, J.; Rojo, T. Sci. 2012, 5, 5884−5901.
[5] Fang, Y.; Xiao, L.; Chen, Z.; Ai, X.; Cao, Y.; Yang, H. Energy Rev. 2018, 1, 294−323.
[6] Wang, T.; Su, D.; Shanmukaraj, D.; Rojo, T.; Armand, M.; Wang, G. Electrochem. Energy Rev. 2018, 1, 200−237.
[7] Hong, H. Y.-P. Mater. Res. Bull. 1976, 11, 173−182.
[8] H. Gao, L. Xue, S. Xin, K. Park, J. B. Goodenough, Angew. Chem. Int. Ed. 2017, 56, 5541– 5545; Angew. Chem. 2017, 129, 5633– 5637.
[9] Z. Zhang, Q. Zhang, J. Shi, Y. S. Chu, X. Yu, K. Xu, M. Ge, H. Yan, W. Li, L. Gu, Y.-S. Hu, H. Li, X.-Q. Yang, L. Chen, X. Huang, Adv. Energy Mater. 2017, 7, 1601196.
[10] Wang Y, Song S, Xu C, et al. Development of solid-state electrolytes for sodium-ion battery‐A short review[J]. Nano Mater. Sci., 2019, 1(2): 91-100.

Stabilising Rh^{4+} Oxides through High Pressure, High Temperature Synthesis

Sean Injac,[1,3] Fabio Denis Romero,[2,3] Masato Goto,[3] and Yuichi Shimakawa.[3]

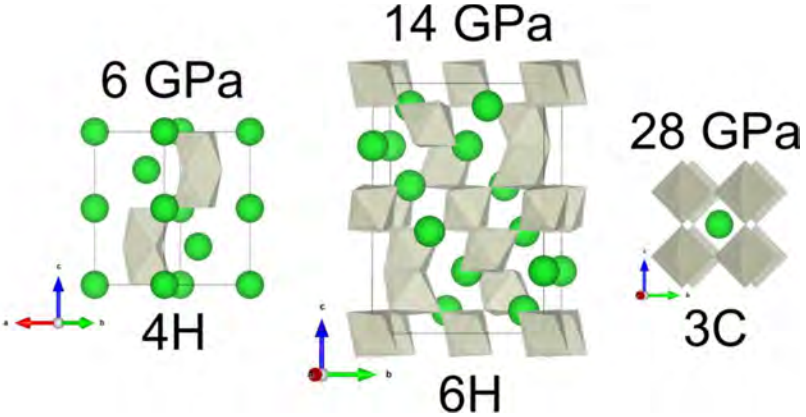
[1] Centre for Science at Extreme Conditions, University of Edinburgh, Scotland, UK

[2] Centre National de Recherche Scientifique, Institut Néel, Grenoble, France,

[3] Institute for Chemical Research, Kyoto University, Kyoto, Japan,

[4] School of Chemistry, The University of Sydney, NSW, Australia.

Synthesis and investigation of Rh containing oxides is of interest in both electronic and magnetic materials, as well as catalytic materials. The $S = ½$ "quantum magnet" state of Rh^{4+} and the competing electronic localisation and delocalisation effects of the 4*d* cations coupled with crystal symmetry effects can lead to complex magnetic and electronic properties. The stabilisation of Rh containing oxide materials is however challenging due to the tendency for Rh oxides to reduce under high temperature conditions. As a result oxides will often contain a mixture of Rh^{3+} ($S = 0$) and Rh^{4+} ($S = ½$).[1] Synthesis under high temperature, high pressure conditions allows for stabilisation of Rh^{4+} oxide materials due to the immense oxidising power of high pressure oxygen at elevated temperatures. The application of synthesis at various pressures results in stabilisation of varying crystal structures depending upon the synthesis pressure, allowing for the investigation of physical properties with varying crystal structures. We have investigated the pressure dependent phase behaviour of the Rh^{4+} perovskite materials $BaRhO_3$ between ambient pressure and 30 GPa.[2] At relatively low pressures oxygen deficient structures are reported, reflecting the presence of Rh^{3+}. Between 6 Gpa and 30 Gpa a structural progression of 4H → 6H → 3C was identified, similar to that reported for other Ba*M*O$_3$ compounds.[3,4] We observe a progression of metallic to semi-metallic properties across the series, reflective of greater electron localisation correlating to the increase proportion of corner sharing RhO_6 octahedral units within the crystal structures.



References

[1] L.T. Nguyen and R.J. Cava, *Chemical Reviews*, 2021, **121**, 2935-2965.

[2] S.D.A. Injac, Y. Xu, F. Denis Romero and Y. Shimakawa, *Dalton Trans.,* 2021, **13**, 4673-4679

[3] Y. Shi, *et al.*, *J. Am. Chem. Soc.,* 2013, **44**, 16507-16516

[4] J-G Cheng, J. Antonio Alonso, E. Suard, J-S Zhou, J.B. Goodenough, *J. Am. Chem. Soc.,* 2009, **21,** 7461-7469

Graphite anodes for Li-ion batteries – an EPR investigation

T. Insinna,[1] E. N. Bassey, [1] K. Märker,[1] A. Collauto,[2] A.-L. Barra,[3] C. P. Grey[1,*]

[1]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom

[2]Pulsed EPR facility, Molecular Sciences Research Hub (Bldg C), 82 Wood Lane, Imperial College London, London, W12 0BZ, United Kingdom

[3]LNCMI-CNRS, 25 Rue des Martyrs, B.P. 166, 38042 Grenoble Cedex 9, France

Graphite is a commercially successful anode for Li-ion batteries: its low cost, low toxicity and high abundance makes it ideally suited for batteries for devices, transportation and grid-based storage. The physical and electrochemical properties of graphite anodes have been thoroughly characterised, but one question remains unanswered—whether the electrons occupy localised states on Li or delocalised states on C, or an admixture therein. In this regard, electron paramagnetic resonance (EPR) spectroscopy is an invaluable tool for characterising the electronic states generated during electrochemical cycling. In this work, *ex situ* variable-temperature (10-300 K), variable-frequency (9-442 GHz) EPR was carried out to extract the *g*-tensors, linewidths, and metallicity of charged graphite at 4 different stages (from least to fully lithiated). We show that at high frequency (>300 GHz), the increased resolution offered by EPR enables up to three different axial environments to be observed, revealing heterogeneity within the graphite particles and the presence of hyperfine coupling to ^{7}Li. Importantly, our work demonstrates the power of EPR spectroscopy in investigating the local electronic structure of graphite on cycling, paving the way for this technique as a tool for screening and investigating novel materials for use in lithium-ion batteries.

Uncovering the S = ½ Kagome Ferromagnet within a Family of Metal-Organic Frameworks

S. A. Ivko,[1] K. Tustain,[2] T. Dolling,[1] A. Abdeldaim,[1,3] O. Mustonen,[1] P. Manuel,[3] C. Wang,[4]
H. Luetkens,[4] and L. Clark.[1]

[1] School of Chemistry, University of Birmingham, UK, [2] Department of Chemistry, University of Liverpool, UK, [3] ISIS Neutron and Muon Source, UK, [4] Paul Scherrer Institut, Switzerland.

Kagome networks of S = ½ magnetic moments are important models in the pursuit of novel quantum materials; lattices of antiferromagnetically coupled moments are hypothesised to host the long-sought quantum spin liquid state,[1] whereas ferromagnetic kagome lattices can display a diverse array of intriguing properties, including formation of topological magnon bands[2] and creation and control of the movement of skyrmions.[3] We have explored a family of Cu^{2+}-containing metal-organic frameworks (MOFs) bearing S = ½ kagome layers pillared by ditopic organic linkers with the general formula $Cu_3(CO_3)_2(x)_3{\cdot}2ClO_4$ (MOF-x), where x is 1,2-bis(4-pyridyl)ethane (*bpe*), 1,2-bis(4-pyridyl)ethylene (*bpy*), or 4,4'-azopyridine (*azpy*).[4] In these materials, Cu^{2+} ions are coordinated to tridentate tris-chelated carbonate ligands in the *ab* plane to form kagome layers that are pillared along the *c* axis by a ditopic organic linker, x. Using single crystal X-ray diffraction we have developed a more chemically intuitive crystal structure for these materials. Conflicting reports on the magnetic ground state of these materials existed in the literature,[5,6] and thus it was unknown whether the underlying model is that of a S = ½ kagome ferromagnet or antiferromagnet. Elucidation of the nature of magnetic exchange in these complex materials requires a variety of complementary experimental techniques. In this work, through the combination of magnetometry, neutron powder diffraction and muon-spin spectroscopy measurements, we show that the magnetic ground state of this family of MOFs consists of S = ½ ferromagnetic kagome layers that are coupled antiferromagnetically via a ten-atom superexchange pathway along the organic pillars.

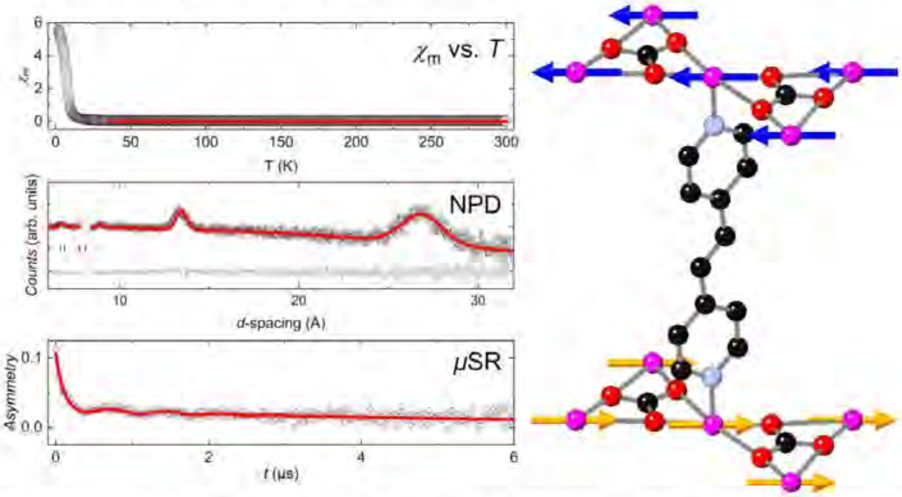


Figure 1: Through a combination of magnetometry, neutron powder diffraction and muon-spin spectroscopy measurements, we show that the ground state in this family of MOFs consists of ferromagnetic kagome layers that are coupled antiferromagnetically along their organic pillaring linkers.

References

[1] C. Broholm *et al.*, *Science*, 2020, **367**, eaay0668. [2] R. Chisnell *et al.*, *Phys. Rev. Lett.*, 2015, **115**, 147201. [3] M. Pereiro *et al.*, *Nat. Commun.*, 2014, **5**, 4815. [4] S. Ivko *et al.*, *Chem. Mater.*, 2022, **34**, 5409. [5] P. Kanoo *et al.*, *Dalton Trans.*, **2009**, 5062. [6] M. O. Ajeesh *et al.*, *Solid State Commun.*, 2015, **207**, 16.

Going off-grid: alternative ways of sampling reciprocal space

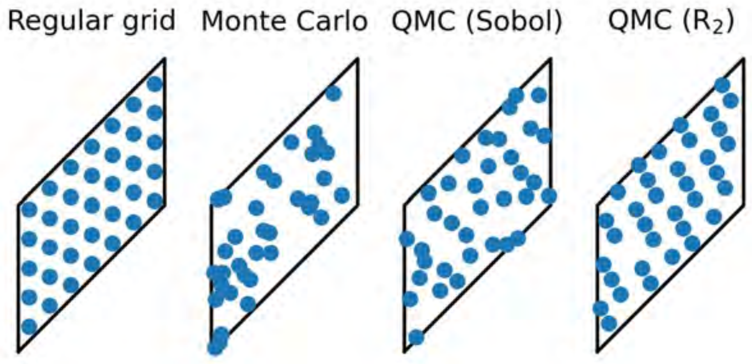
Adam J. Jackson[1]

[1] Theoretical and Computational Physics Group, Scientific Computing Department, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell, UK

Solid-state chemistry research makes heavy use of simulations in which extended systems are represented by a crystalline unit cell and periodic boundary conditions. For the evaluation of ground-state forces, optical properties and thermodynamic potentials expensive or diverging real-space expansions can be replaced by manageable reciprocal-space integrals. However, ensuring numerical convergence of these Brillouin-zone (BZ) summations can be tricky. The most popular sampling scheme, supported by almost every periodic quantum chemistry or lattice dynamics code, is regular grid sampling along Monkhorst-Pack divisions or with an additional shift to include or exclude the Gamma-point. This has been extended in a generalised approach by allowing alternative basis vectors to be considered in order to minimise the number of required samples at a given level of packing after symmetry operations are considered.[1,2]

Outside of computational materials science, Monte Carlo sampling (using random numbers) and Quasi-Monte Carlo (QMC) sampling (using number sequences with suitable sampling properties) are applied to a range of difficult sampling problems. Quasi-random sampling schemes have already been applied successfully to spherical averaging for simulation of inelastic neutron scattering spectra from powders.[3,4] When applying such schemes to BZ integration, the number of samples cannot be symmetry-reduced at all – but every sample adds new information to the averages. In this work we examine the performance of these schemes for a variety of density-functional theory and lattice dynamics calculations, finding that in many cases the QMC sampling converges smoothly and quickly compared to traditional methods. Simplified sampling schemes and uncertainty analysis have potential applications in high-throughput studies and in improving the usability of simulation methods for non-specialists.

A 2-D schematic of various reciprocal-cell sampling schemes with an equal number of points



References

[1] J. Moreno and J. M. Soler, *Physical Review B*, 1992, **45**, 13891.

[2] W. S. Morgan, J. J. Jorgensen, B. C. Hess and G. L. W. Hart, *Computational Materials Science,* 2018, **153**, 424.

[3] S. Toth, W. Wu, D. T. Adroja, S. Rayaprol and E. V. Sampathkumaran, *Physical Review B*, 2016, **93**, 174422.

[4] R. Fair, A. J. Jackson, D. Voneshen, D. Jochym, D. Le, K. Refson, T. G. Perring, *Journal of Applied Crystallography,* 2022 *(Accepted)*

Cobalt substitution in beta-tricalcium phosphate for biomaterial applications

Chandrakant Jadhav,[1,2] Jo Duncan,[1,2] Iain Gibson[1,3] Jan Skakle.[1,2]

[1] Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland UK

[2] Department of Physics, University of Aberdeen, Aberdeen AB24 3UE, Scotland UK

[3] Institute of Medical Sciences, University of Aberdeen, Aberdeen AB22 ZD, Scotland UK

β-tricalcium phosphate (β-$Ca_3(PO_4)_2$; β-TCP) is an essential reactant phase in one of the most prevalent calcium phosphate cement (CPC) systems. These cements are extensively used in orthopaedic surgery to repair bone. β-TCP may undergo cationic substitution (Ca^{2+}) with a wide range of ions including monovalent (Na^+, K^+)[1], divalent (Sr^{2+}, Zn^{2+})[2] and trivalent (Fe^{3+}, Ga^{3+})[3] cations in its lattice without significant structural distortion Substituting Mg or small amounts of monovalent ions has been shown to improve the mechanical strength of β-TCP4

Cobalt ions incorporated into inorganic biomaterials have been shown to have angiogenic and antimicrobial properties; they stimulate blood vessel formation and inhibit bacteria, respectively. These properties can play an important role in bone substitute materials. However, the cobalt content must be controlled since high concentrations are toxic[5].

In this study, we investigated the substitution limit of Co-β-TCP synthesised by the solid-state method using XRD, FTIR, UV-VIS, SEM and EDX. β-TCP with different amounts of Co^{2+} were synthesised and XRD showed a secondary phase appearing above x=0.4, Up to this level, unit cell parameters **a** and volume V decreased linearly, however unit cell parameter **c** decreased linearly up to x~0.3 and then increased up to x~0.5 after which it remained constant, indicating the limit of the solid solution.

The crystal structure was refined using GSAS-2. β-TCP has a relatively large hexagonal structure; there are 5 unique Ca sites, 3 P sites and 18 O sites. Co^{2+} was shown to be preferentially incorporated at the Ca(5) side as indicated initially by U_{iso} values and then by refining the occupancy. This is similar to what is observed in the Cu system.

Bond Valence Sum (BVS) calculations shows good agreement with previously reported results for undoped β-TCP[6]. BVS for Co^{2+}-substituted β-TCP compounds were studied, which shows significant variation on Ca(5) site as Co^{2+} ions substitute preferentially on that site. Ellipsoidal analysis using PIEFACE[7] from β-TCP and its compositions with cobalt shows the highest distortion on Ca(5) and Ca(4) sites.

FTIR analysis showed that cobalt substitution generally resulted in a decrease in resolution of the phosphate bands, and a peak shift of some of the ν_3 bands to lower wavenumbers.

References

[1] S. Quillard et al. Acta Biomater, 2011, **7**, 1844–1852.

[2] K. Yoshida et al, Journal of the American Ceramic Society, 2005, **88**, 2315–2318.

[3] L. Sinusaite et al, Materials Science and Engineering C, 2020,**112**,110918.

[4] K. Narita et al, J Biomedical Materials Research B: Applied Biomaterials, 2019,**107**, 2238–2253,

[5] M. Zhang et al, Journal of Materials Chemistry, 2012, **22**, 21686–21694,

[6] M. Yashima et al, Journal of Solid State Chemistry 2003,**175**, 272-277

[7] J. Cumby and J. Paul Attfield, Nature Communications, 2017, **8,** 14235

Investigating $NaGeSbO_5$ as a transparent thermoelectric

Xiaoyu Jia,[1,2] Joe Willis[1,2] and David Scanlon.[1,2]

[1] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom,

[2] Thomas Young Centre, University College London, Gower Street, London, WC1E 6BT, United Kingdom.

Transparent conducting oxides (TCOs) are a unique class of oxide materials that exhibit both transparency and electronic conductivity simultaneously. Thermoelectrics (TEs) are a class of materials that can directly convert heat and electricity mutually. Their Seebeck effect allow thermoelectric devices to recover waste heat and convert it into electrical power. The discovery of high performance transparent thermoelectric materials can potentially develop novel applications such as smart windows and screens with energy harvesting, cooling, and thermal sensing functionalities.

In this project, $NaGeSbO_5$ was chosen due to its complex crystal structure, which normally yields low lattice thermal conductivities, and the $(n-1)d^{10}ns^0sp^0$ electronic configuration of Ge(IV) and Sb(V) which should yield a dispersive conduction band minimum, similar to the known TCOs. State-of-the-art ab initio calculations were performed using the VASP code to understand its thermoelectric ability. We firstly calculated the thermodynamic stability versus known compounds within Na-Ge-Sb-O phase space using CPLAP,[1] we studied the geometry and band structure of $NaGeSbO_5$ and found its band gap is wide enough to ensure optical transparency. Following this, we calculated its phonon band structure using phonopy [2] and its electron transport properties using AMSET.[3] We also calculated the band alignment to test the doping preference of the material using SURFAXE.[4] In the future, we will continue to study its lattice thermal conductivity, predict the figure of merit ZT and investigate the defect chemistry.

References

[1] J. Buckeridge, D. O. Scanlon, A. Walsh, C. R. A. Catlow, *Computer Physics Communications*, 2014, **185**, 330.

[2] A. Togo, I. Tanaka, *Scripta materialia*, 2015,**108**, 1359.

[3] A. M. Ganose, A. J. Jackson, D. O. Scanlon, *Nat. Commun.*, 2021,**12**, 2222.

[4] K. Brlec, D. Davies, D. O. Scanlon, *Journal of open source software*, 2021,**6**, 3171.

Pillared Vanadium Molybdenum Disulfide Nanosheets; a High-performance Cathode for Magnesium-ion Batteries

Pengcheng Jing,[1] Duncan H. Gregory.[1]

[1] *School of Chemistry, University of Glasgow, Glasgow G12 8QQ*

Although lithium-ion batteries (LIBs) have been recognised as high energy density and durable energy storage devices, the scarcity of lithium resources and potential safety issues originating from dendrite growth and thermal runaway are causes for concern.[1-2] By contrast to lithium, magnesium resources are relatively abundant and so novel magnesium-ion batteries (MIBs), which can operate safely (due to dendrite-free Mg plating) and in principle carry twice as much charge, have been proposed to supplement and/or replace LIBs.[3-4] If MIBs are to be seriously considered for next-generation energy storage then a number of major obstacles need to be overcome. The lack of reversible cathode materials with sufficient capacity and cycle life is one of these challenges.

We have investigated vertically stacked vanadium molybdenum sulfide (VMS) nanosheets towards the design of a new cathode material for MIBs. The material is synthesised via a simple hydrothermal reaction followed by a mild heat treatment. The structure, electrochemical performance, and Mg^{2+} cation storage mechanism of the VMS nanosheets were studied (Figure 1). The material features improved electronic conductivity via vanadium integration within molybdenum disulfide nanostructures. Moreover, improved Mg^{2+} cation diffusion can be achieved via electrolyte-additive-induced interlayer expansion. As a result, the VMS nanosheets are capable of exhibiting capacities of 211.3 mA h g^{-1} and 144.5 mA h g^{-1} at current densities of 100 mA g^{-1} and 1000 mA g^{-1}, respectively. The VMS nanosheets also demonstrate long-term cycling stability, retaining 82.7 % of the maximum capacity after 500 cycles at a current density of 1000 mA h g^{-1}. These results suggest that VMS nanosheets could be promising candidates for high-performance cathodes in MIBs.

Figure 1. (a) X-ray diffraction patterns of VMS, VS_2, and MoS_2, (b) scanning electron microscopy image of VMS, and (c) galvanostatic cycling performance of VMS, VS_2, and MoS_2 at a current density of 100 mA g^{-1}.

References

[1] G. Zubi, R. Dufo-López, M. Carvalho, G. Pasaoglu, *Renewable Sustainable Energy Rev.*, 2018, **89**, 292-308.

[2] L. Kong, Y. Li, W. Feng, *Electrochem. Energy Rev.,* 2021**, 4 (4)**, 633-679.

[3] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature* 2000**, 407 (6805)**, 724-727.

[4] M. Mao, T. Gao, S. Hou, C. Wang, *Chem. Soc. Rev.* 2018**, 47 (23)**, 8804-8841.

Frenkel Excitons in Vacancy-ordered Titanium Halide Perovskites (Cs_2TiX_6)

Seán R. Kavanagh,[1,2] Shanti Liga, [3] Christopher N. Savory,[1] Gerasimos Konstantatos,[3,5] Aron Walsh, [2,4] David O. Scanlon[1]

[1] Thomas Young Centre and University College London, London, UK

[2] Thomas Young Centre and Imperial College London, London, UK

[3] ICFO-Insitut de Ciencies Fotoniques, The Barcelona Institute of Science and Technology, Casteldefels, 08860 Barcelona, Spain.

[4] ICREA-Institució Catalana de Recerca i Estudia Avançats, Lluis Companys 23, 08010 Barcelona, Spain.

Low-cost, non-toxic and earth-abundant photovoltaic materials are a long-sought target in the solar cell research community. Perovskite-inspired materials have emerged as promising candidates for this goal, with researchers employing materials design strategies including structural, dimensional and compositional transformations to avoid the use of rare and toxic elemental constituents, while attempting to maintain high optoelectronic performance.[1,2]

These strategies have recently been invoked to propose Ti-based vacancy-ordered halide perovskites (A_2TiX_6; A = CH_3NH_3, Cs, Rb, K; X = I, Br, Cl) for photovoltaic operation,[3-5] following the initial promise of Cs_2SnX_6 compounds. Theoretical investigations of these materials, however, consistently overestimate their band gaps – a fundamental property for photovoltaic applications.

Here,[6] we reveal strong excitonic effects as the origin of this discrepancy between theory and experiment; a consequence of both low structural dimensionality and band localization. These findings have vital implications for the optoelectronic application of these compounds, while also highlighting the importance of frontier-orbital character for chemical substitution in materials design strategies. This work reveals the critical role of cation disorder in the photovoltaic performance of these systems, alongside key considerations for future research in this area.

References

[1] Huang, Y.-T.; Kavanagh, S. R.; Scanlon, D. O.; Walsh, A.; Hoye, R. L. Z. Perovskite-Inspired Materials for Photovoltaics and beyond—from Design to Devices. *Nanotechnology* **2021**, *32* (13), 132004

[2] Wang, Y. ‡ & Kavanagh, S. R. ‡; Burgués-Ceballos, I.; Walsh, A.; Scanlon, D.; Konstantatos, G. Cation Disorder Engineering Yields AgBiS2 Nanocrystals with Enhanced Optical Absorption for Efficient Ultrathin Solar Cells. *Nat. Photon.* **2022**, *16* (3), 235–241

[3] Chen, M.; Ju, M.-G.; Carl, A. D.; Zong, Y.; Grimm, R. L.; Gu, J.; Zeng, X. C.; Zhou, Y.; Padture, N. P. Cesium Titanium(IV) Bromide Thin Films Based Stable Lead-Free Perovskite Solar Cells. *Joule* **2018**, *2* (3), 558–570.

[4] Euvrard, J.; Wang, X.; Li, T.; Yan, Y.; Mitzi, D. B. Is Cs2TiBr6 a Promising Pb-Free Perovskite for Solar Energy Applications? *J. Mater. Chem. A* **2020**, *8* (7), 4049–4054.

[5] Cucco, B.; Bouder, G.; Pedesseau, L.; Katan, C.; Even, J.; Kepenekian, M.; Volonakis, G. Electronic Structure and Stability of Cs2TiX6 and Cs2ZrX6 (X = Br, I) Vacancy Ordered Double Perovskites. *Appl. Phys. Lett.* **2021**, *119* (18), 181903.

[6] Kavanagh, S. R.; Savory, C. N.; Liga, S. M.; Konstantatos, G.; Walsh, A; Scanlon, D. O. Frenkel Excitons in Vacancy-ordered Titanium Halide Perovskites (Cs_2TiX_6). *Journal of Physical Chemistry Letters* **202**

Synthesis of new layered oxychalcogenides in the AM_2Q_2O system

Nicola. D. Kelly[1] and Simon J. Clarke[1]

[1] Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford,
United Kingdom.

Layered cuprates such as $YBa_2Cu_3O_{7-x}$ exhibit unconventional high-temperature superconductivity as a result of the CuO_2 square planes within their crystal structures. Recently, superconductivity has been discovered in the layered oxypnictides $BaTi_2Bi_2O$ and $BaTi_2Sb_2O$ which contain "anti-CuO_2" transition metal-oxide square layers, i.e. Ti_2O.[1] Doping of these materials on the Ba site enhances T_c,[1] which led researchers to investigate other ways to apply chemical pressure to these systems through isovalent or aliovalent substitution. In this way, five transition metal oxychalcogenides containing an M_2O square net were discovered with the general formula AM_2Q_2O where A is an alkali metal (K, Rb or Cs), M is a transition metal (Ti or V), and Q is a chalcogen (S, Se or Te).[2-6] The transition metal cations have average oxidation state +2.5 on a single crystallographic site, producing metallic conductivity and temperature-independent paramagnetism. Here we report the solid-state synthesis and characterisation of the remaining thirteen compositions in the AM_2Q_2O structural family, **Fig. 1**. We also present initial results on a novel van der Waals layered material, Ti_2Te_2O, synthesised via a soft chemical approach.

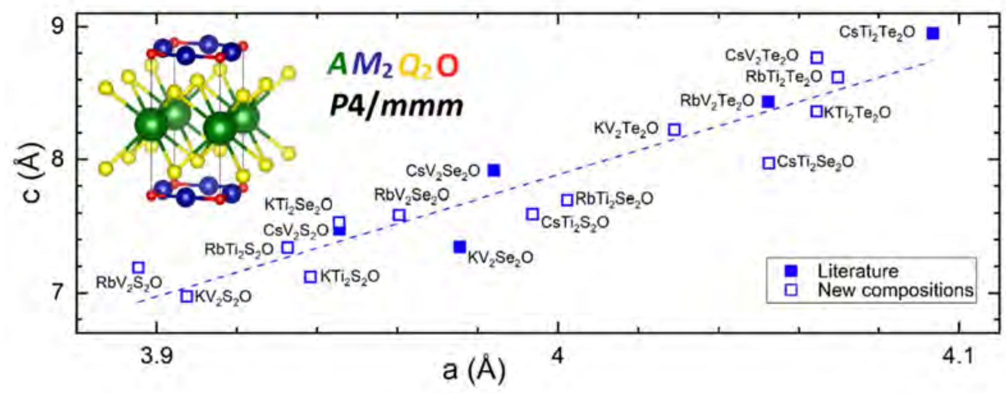


Fig. 1. Lattice parameters of the AM_2Q_2O compounds where A is an alkali metal (K, Rb or Cs), M is a transition metal (Ti or V), and Q is a chalcogen (S, Se or Te). Inset: unit cell of AM_2Q_2O.

References

[1] T. Yajima. *Condens. Matter,* 2017, **2**, 4.

[2] H. Lin, J. Si, X. Zhu, K. Cai, H. Li, L. Kong, X. Yu and H.-H. Wen, *Phys. Rev. B*, 2018, **98**, 075132.

[3] M. Valldor, P. Merz, Y. Prots and W. Schnelle, *Eur. J. Inorg. Chem*. 2016, **2016**, 23.

[4] M. Valldor, P. Merz, Y. Prots, Y. Watier and W. Schnelle, *Inorg. Chem.* 2016, **55**, 11337.

[5] A. Ablimit, Y.-L. Sun, H. Jiang, S.-Q. Wu, Y.-B. Liu and G.-H. Cao, *Phys. Rev. B,* 2018, **97**, 214517.

[6] Z. Guo, F. Sun, D. Puggioni, Y. Luo, X. Li, X. Zhou, D. Y. Chung, E. Cheng, S. Li, J. M. Rondinelli, W. Yuan and M. G. Kanatzidis, *Chem. Mater.* 2021, **33**, 2611.

Identification of Glass Transition in Glassy Titanium-based MOFs

A. Kono,[1] and T. D. Bennett[2]

[1]University of Cambridge, UK and ENEOS Corporation, Japan,
takeshita.ayano@eneos.com,

[2] University of Cambridge, UK, tdb35@cam.ac.uk

Metal-organic framework (MOF) glasses are emerging as distinct category of metallic, organic and inorganic glasses. MOF glasses are amorphous solids, which are induced mainly by the structural collapse of crystalline MOFs via melt-quenching, heating, high-pressure or mechanochemical methods. Reports of the direct-synthesis of MOF glasses are limited. Zhao et al., reported the transparent glassy titanium-based MOFs, which were synthesized by dissolving the titanium nodes and organic linker in the solvent modulator to form a liquid, and following removal of the solvent from the liquid via evaporation.[1]

The synthesis pathway is similar to the inorganic sol-gel process, in that a network is formed in solution and the configurational freedom decreases by removal of the solvent. In the case of sol-gel process derived silica-based glasses, further densification occurs on calcination, resulting in the gel to glass conversion. In the densification process of silica-based glasses, structural relaxation and polymerization occur simultaneously, making it difficult to observe the glass transition endotherm of the gels, while the glass transition behaviour can be observed once the material is fully densified.[2]

The glass transition behaviour of directly synthesized glassy titanium-based MOFs itself has not been reported so far for similar difficulty in characterization. In this study, we synthesized transparent glassy MOFs, based on the literature[1] and thermogravimetric analysis and different scanning calorimetry analysis were performed to evaluate the thermal properties of glassy MOFs. The glassy titanium-based MOFs showed gradual mass losses at relatively low temperatures, and it is indicated that the temperature of structural relaxation and polymerization / thermal degradation might overlap. Therefore, fast scanning calorimetry was used to attempt to analyse the glass transition behaviour. Through fast heating rates, the sample can be heated up to high temperatures for a short time; thus, it is expected to avoid thermal decomposition, which might affect the observation of glass transition behavior. This method has been used to observe the glass transition temperature of polymers with intrinsic microporosity (PIMs) with a small number of conformational degrees of freedom.[3] By using fast scanning calorimetry, we were able to observe the glass transition behavior. Further understanding of the thermal property of MOF glasses, which are synthesized at low temperatures, may be useful to envision several applications such as gas separation membranes.

References

[1] Z. Yingbo, S. Y. Lee, N. Becknell, O. M. Yaghi, and C. A. Angell, *J. Am. Chem. Soc.*, 2016, **138,** 10818.

[2] C. J. Brinker, G. W. Scherer, E. P. Roth, *J. Non. Cryst. Solids.*, 1985, **72**, 345.

[3] H. Yin, Y. Z. Chua, B. Yang, C. Schick, W. J. Harrison, P. M. Budd, M. Böhning, A. Schönhals, *J. Phys. Chem. Lett.*, 2018, **9**, 2003.

Anharmonic lattice dynamics of superionic lithium nitride

Gabriel Krenzer,[1] Chang-Eun Kim,[2] Kasper Tolborg,[1] Benjamin Morgan,[3] Aron Walsh.[1]

[1] Imperial College London,

[2] Lawrence Livermore National Laboratory,

[3] University of Bath.

Ionic transport in conventional solids is usually considered as being effected by a sequence of discrete "hops".[1, 2] While this model is usually appropriate for ionic solids with low-to-medium ionic conductivities, fast ionic conduction is often associated with highly-concerted ionic motion 2, 11-15. This correlation between fast-ion conduction and cooperative ion-transport mechanisms suggests that ionic motion in superionic conductors might be better described in terms of collective degrees of freedom, rather than independent single-atom coordinates 16. One appealing choice of basis is the set of normal modes of vibration. Any changes in vibrational properties across the superionic transition may also provide insights into the underlying physics of this phenomenon. We assess harmonic, quasi-harmonic, and anharmonic descriptions of the phonons of Li3N. The harmonic and quasi-harmonic models show no change in features across the superionic transition. The anharmonic model exhibits a breakdown for all modes. The implications for developing lattice-dynamics-based-descriptors for superionic conductors as well as the application of machine learning force to simulate diffusive properties are discussed.

References

[1] G. H. Vineyard *et al.*, *J. Phys. Chem. Solids*, 1957, **3**, 121-127.

[2] C. R. A. Catlow, *Solid State Ionics*, 1983, **3**, 89-107.

[3] H. Zhang ***et al.***, *J. Chem. Phys.*, 2019, **3**, 174506.

[4] M. Xu *et al.*, *Appl. Phys. Letters*, 2012, **3101**, 031901.

[5] M. Burbano *et al.*, *Phys. Rev. Lett.*, 2016, **3**, 135901.

[6] B. J. Morgan, *Solid State Ionics*, 2021, **33**, 2004-2018.

[7] X. He *et al.*, *Nat Commun.*, 2017, **8**, 1-7.

[8] N. Molinari *et al.*, *Phys. Rev. Lett.*, 2021, **127**, 025901.

Simulating volatile fission products in U(Pu)N and corresponding oxides

Navaratnarajah Kuganathan and Robin W. Grimes

Department of Materials, Imperial College London, London, SW7 2AZ, United Kingdom

Volatile fission products (Kr, Xe, Br, I, Te, Rb and Cs) formed during normal reactor operation initially occupy defect sites and affect the performance of nuclear fuel, particularly at high levels of burn up.[1] Using spin polarised density functional theory, we examined the incorporation of volatile fission products in a range of interstitial and defect sites in UN and PuN. These were compared to equivalent results for UO_2 and PuO_2. Both Kr and Xe exhibit endothermic incorporation energies at all defect sites in nitrides.[2] The least unfavourable site for all fission products is the di-vacancy cluster (since it has the greatest volume). There is a preference for the accommodation of fission products, with the exception of Te, in PuN than UN. Considerable differences were noted in the incorporation between oxides and nitrides leading to distinct fission product retention behaviour.[2] Specifically, both Kr and Xe are considerably less unfavourable in the oxides than nitrides. The same preference in the oxides is predicted for I and especially Rb and Cs and to a lesser extend Br.[2] While Te shows a preference for PuN over PuO_2, there is a small preference for UO_2 over UN.

References

[1] J. Rest, M.W.D. Cooper, J. Spino, J.A. Turnbull, P. Van Uffelen, C.T. Walker, *Journal of Nuclear Materials*, 2019, **513**, 310-345.

[2] N.Kuganathan, N. J. Barron, R. W. Grimes, *Journal of Nuclear Materials* (under review).

In situ grain mapping of hybrid improper ferroelectrics under applied electric fields

Evie Ladbrook[1], Stefano Checchia[2] and Mark S. Senn[1]

[1]University of Warwick, Coventry, United Kingdom

[2]ESRF, 38000, Grenoble, France

3DXRD (also referred to as diffraction resolved tomography) is a powerful technique to study polycrystalline electronic materials on a grain-by-grain basis. A grain map of the sample can be generated where each grain is characterised by its position, shape, orientation, and strain.[1] Knowledge of the microstructure of such materials under an applied field is incredibly valuable in understanding and subsequently tuning the bulk properties. This work presents an *in situ* 3DXRD experiment performed on polycrystalline hybrid improper ferroelectric (HIF) under applied electric field.

There is growing excitement around HIFs due to their potential as Pb-free multiferroics, owing to the versatility of their design criteria in contrast to proper ferroelectrics which require Jahn-Teller active cations. Instead, the polarisation in HIFs arises from coupling of a polar mode to two non-polar distortions, such as octahedral rotations. However, compared to proper ferroelectrics, where polarisation is the primary order parameter, little is currently understood about the domain structure and polarisation switching mechanism. The current work builds upon an *in situ* X-ray diffraction study on HIF, $Ca_{2.15}Sr_{0.85}Ti_2O_7$, which demonstrates the structural response to an applied electric field and indicates a preferred switching pathway.[2] 3DXRD was utilised to image individual grains as an electric field is applied and reversed, thereby collecting data throughout the switching process. As shown in Figure 1, we have achieved a grain reconstruction for bismuth ferrite, as a prototypical example, and are developing a robust method for the lower symmetry, $Ca_{2.15}Sr_{0.85}Ti_2O_7$. A significant focus of this work was on optimising this technique, due to the complex experimental set up and sample design as shown in Figure 1, and subsequent analysis for HIFs and other materials.

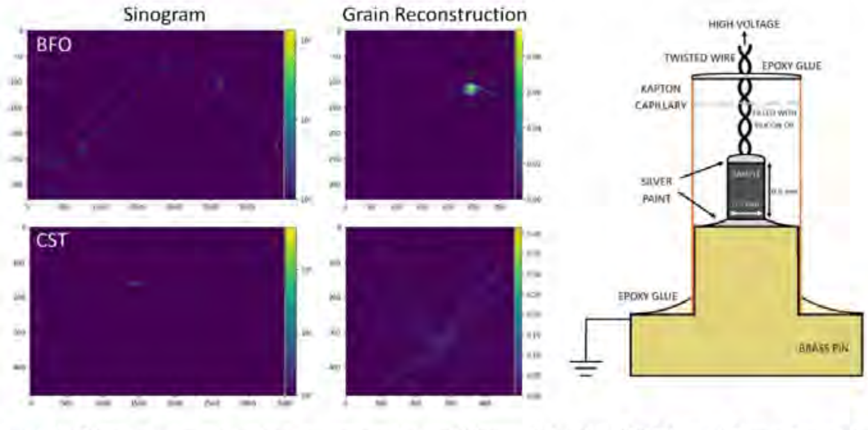


Figure 1. Left: Sinogram and grain reconstruction of bismuth ferrite (BFO) and $Ca_{2.15}Sr_{0.85}Ti_2O_7$ (CST), showing a partial reconstruction as compared to BFO. Right: Schematic of sample cell.

References

[1] J. Oddershede *et. al.*, *J. Appl. Cryst.*, 2015, **48**, 882-889.

[2] G. Clarke, C. Ablitt, J. Daniels, S. Checchia and M. S. Senn, *J. Appl. Cryst.*, 2021, **54**, 533-540.

Computational modelling of post transition metal oxide Sb_2O_5

Ke Li[ab], Joe Willis[ab] and David O. Scanlon[ab]

[a]Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

[b]Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, United Kingdom

Transparent conducting oxides (TCOs) uniquely display optical transparency and electrical conductivity in a single material, enabling them indispensable in modern optoelectronics and power electronics applications [1]. However, a heavy dependence on a small number of post- transition metal TCOs places limitations on the number and type of devices that they can support. Therefore, discovering more wide band gap (WBG) oxides that can be doped to display metallic conductivity is a great challenge in the field.

Herein, we use density functional theory to explore an underexplored binary post-transition metal oxide Sb_2O_5. We determine the most suitable functional for calculations by comparing the relaxed crystal structures, electronic structures, and optical absorption spectra [2]. We use the hybrid functional PBE0 to illustrate the thermodynamic stabilities of the competing phases. We carry out charge transport properties using the AMSET code where the carrier mobility and scattering rates can be determined from first principles calculations [3]. In addition, we aim to present a defect analysis and identify the defect that can achieve maximum conductivity in Sb_2O_5.

[1] A. J. Jackson et al., 'Computational Prediction and Experimental Realization of Earth-Abundant Transparent Conducting Oxide Ga-Doped $ZnSb_2O_6$', ACS Energy Lett., pp. 3807–3816, Oct. 2022, doi: 10.1021/acsenergylett.2c01961.

[2] J. P. Allen, J. J. Carey, A. Walsh, D. O. Scanlon, and G. W. Watson, 'Electronic Structures of Antimony Oxides', J. Phys. Chem. C, vol. 117, no. 28, pp. 14759–14769, Jul. 2013, doi: 10.1021/jp4026249.

[3] A. M. Ganose, J. Park, A. Faghaninia, R. Woods-Robinson, K. A. Persson, and A. Jain, 'Efficient calculation of carrier scattering rates from first principles', Nat Commun, vol. 12, no. 1, p. 2222, Dec. 2021, doi: 10.1038/s41467-021-22440-5.

Thermal broadening in core level and valence band XPS

Roxy Lee,[1] Mark Isaacs[1] and Robert Palgrave.[1]

[1] Univ. College London (United Kingdom),

One of the major contributors to the XPS lineshape is thermal broadening of the ground state, in addition to the linewidth of the exciting radiation, the spectrometer resolution, hole lifetime in the sample, inelastic scattering of photoelectrons and final state effects.[1] The effect of thermal broadening on the linewidth of core level and valence band spectra was explored for the series of bismuth oxy halides; an emerging class of materials exhibiting photocatalytic properties:[2] BiOCl, BiOBr and BiOI and related compounds. Variation in temperature from -100 °C to +100 °C led to changes in the linewidths for both core level and valence band spectra depending on the halide ion.

Interpretation of the valence band region was supported by theoretical spectra, simulated using density functional theory. To compare with the experimental spectra, the calculated density of states were corrected using photoionization cross-section parameters, a zero-point binding energy shift was applied to bring the DFT and XPS spectra into alignment, and Gaussian and Lorentzian spectral broadening was applied. The thermal broadening contribution to the total broadening of the theoretical DoS was estimated by fitting the simulated and experimental spectra.

References

[1] C. S. Fadley and D. A. Shirley, *Journal of research of the National Bureau of Standards. Section A, Physics and Chemistry*, 1970, **74A**, 543-558.

[2] X. Wei, M. U. Akbar, A. Raza and G. Li, *Nanoscale Advances*, 2021, **3**, 3353-3372.

From cubic to hexagonal: electronic trends across metal halide perovskite polytypes

Zhenzhu Li,[1] Ji-Sang Park[2], Alex M. Ganose[1], Aron Walsh.[1]

[1] Imperial College London

[2] Sungkyunkwan University

Polytypes formed during the growth of metal halide perovskites can give rise to the formation of impurity face-sharing sequences in a corner-sharing network. Here, the electronic influences of such phases are found to be closely correlated with the ratio and stacking sequence of the face-sharing layers. The band gaps of polytypes feature a characteristic evolution from indirect to direct band gap from pure hexagonal phase to pure cubic phase. Rather than arising from the orbital mixing at the atomic level, a strong band gap bowing factor of 1.96 eV was attributed to the long range electronic interaction between the octahedral building blocks. While retaining a high carrier velocity, Fermi surface analysis further revealed a decrease of dimensionality from 3D to 2D in frequently observed polytypes, indicating a carrier blocking and anisotropic carrier transport effect of the as-formed hexagonal impurity phases.

References

[1] Zhenzhu Li, et al., *Chem. Sci.* 2021, **12**, 12165-12173.

[2] Ji-Sang Park, et al., *ACS Energy Lett.* 2020, **5**, 2231−2233.

Dynamic Analysis of Hybrid Lead Halide Perovskites

Xia Liang,[1] Zhenzhu Li,[1] and Aron Walsh[1]

[1] Imperial College London.

Hybrid lead halide perovskite materials with an empirical formula of ABX_3 have attracted great interest in the solar energy conversion community, because of their high power conversion efficiency, relatively low processing cost, and potential to be employed in tandem solar cells due to band gap tunability[1]. However, there are still several major challenges to be tackled before their commercialisation, the first of which is its phase instability under ambient temperature with an undesired phase transition into low-efficiency phases. Molecular dynamics (MD) is a natural choice for simulating these phase transition behaviours at the atomic scale, and the recent emergence of machine learning potential (MLP) methods enables large-scale MD simulation with density functional theory level accuracy. This work utilised an existing kernel-based machine learning force field method[2] to produce MD trajectories, and developed a quantitative analysis method to study the dynamic properties of three lead halide perovskite materials with Cs, methylammonium (MA) and formamidinium (FA) A-sites. The dynamic analysis covers a wide variety of properties, including pseudo-cubic lattice parameters, octahedral tilting and distortion, molecular orientation and displacement, as well as the spatial correlation of these properties. A spontaneous tilting pattern is found in the alpha phase of MA-containing compounds, that is not discovered in the other two materials. This tilting behaviour distinguishes $MAPbI_3$ from the other two perovskites, which do not possess stable black phase at room temperature.[3] This combination of MLP methods with dynamic property analysis has shown great potential on studying realistic behaviours of perovskite materials and is easily transferable to more complicated structures.

References

[1] J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon. M. van Schilfgaarde and A. Walsh, Nano Letters 2014, **Vol. 14**, Pages 2584-2590

[2] R. Jinnouchi, K. Miwa, F. Karsai, G. Kresse and R. Asahi, The Journal of Physical Chemistry Letters 2020, **Vol. 11**, Pages 6946-6955

[3] T. A. S. Doherty, S. Nagane, D. J. Kubicki, Y.-K. Jung, D. N. Johnstone, A. N. Iqbal, et al, Science 2021, **Vol. 374**, Pages 1598-1605

Enhanced photoluminescence and reduced dimensionality via vacancy ordering in a 10H halide perovskite

Hang Liu,[1] Hassan Hafeez,[2] David B. Cordes,[1] Alexandra M. Z. Slawin,[1] Gavin Peters,[1] Stephen Lee,[3] Ifor D.W. Samuel,[2] Finlay D. Morrison.[1]
[1] EaStCHEM School of Chemistry, University of St. Andrews, North Haugh, St Andrews KY16 9ST, UK,
[2] Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St Andrews, North Haugh, St. Andrews KY16 9SS, UK,
[3] School of Physics and Astronomy, SUPA, University of St. Andrews, North Haugh, St. Andrews KY16 9SS, UK.

In the past decade, both inorganic and organic-inorganic hybrid halide perovskites have generated immense research interest for application in optoelectronic devices because of their favourable electronic structure, structural tunability and low cost of fabrication.[1] B-site vacancy ordered halide perovskite, with general formula $A\square_nB(II)'_{1-3n}B(III)_{2n}X_3$ (n represents the fraction of vacancies per perovskite formula unit), was re-visited to investigate the relationship between the crystal and electronic structure. Typical studies involving $n = 0.25$ $Cs_4CuSb_2Cl_{12}$ and $n = 0.33$ $Cs_3Sb_2Cl_9$ demonstrated the potential application in the fabrication of solar cell absorber and photodetector device.[2, 3] By varying n, a series of potential new compounds and structures with varying octahedral connectivity can be generated and which is dependent on the extent and configuration of vacancy distribution as well as the AX_3 packing sequence of the lattice.

In this work, we report a synthesis of one-dimensional, $n = 0.3$ vacancy-ordered perovskite $Cs_{10}MnSb_6Cl_{30}$ with a distinctive 10H-type structure and $(hcccc)_2$ stacking sequence. The vacancy ordering at the B-site reduces the dimensionality to 1D resulting in enhanced photoluminescence in comparison to the previously reported 25% vacancy-ordered 3C polytype $Cs_4MnSb_2Cl_{12}$ with 2D connectivity.[2] This work not only reports the existence of the 10H structure in halide perovskites but also demonstrates B-site deficiency and stacking sequence variation as a direction to tune the optical properties of perovskite polytypes via vacancy rearrangements.

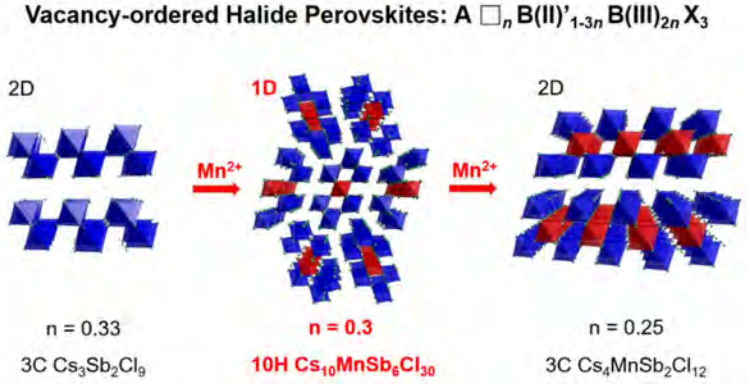


Figure 1 Schematic figure for the structural relationship between vacancy distribution and dimensionality in vacancy ordered halide perovskite

References

[1] B. Saparov and D. B. Mitzi, Chem. Rev., 2016, 116, 4558-4596.
[2] B. Vargas, R. Torres-Cadena, and et al., Chem. Mater., 2018, 30, 5315-5321.
[3] A. K. Pramod, M. Raj Subramaniam, S. A. Hevia and S. K. Batabyal, Mater. Lett., 2022, 306.

Phase transitions and optical properties of the trigonal perovskite $(CH_3NH_3)_2TeCl_6$

Y. Liu[1], J.K. Cockcroft[1], Z. Chen[2], M.A. Hayward[2], P.F. Henry[3,4], R.S. Perry[3,5] and R.G. Palgrave[1]

[1] Department of Chemistry, University College London, UK,

[2] Department of Chemistry, University of Oxford, UK,

[3] ISIS Facility, Rutherford Appleton Laboratory, UK

[4] Department of Chemistry, Ångström Laboratory, Sweden

[5] London Centre for Nanotechnology, University College London, UK

Metal halide perovskites are receiving attentions in the photovoltaic field. The vacancy-ordered double-perovskite A_2BX_6, which is obtained by replacing half of the B-site cations with vacancies inside a doubled ABX_3 unit cell, is greatly researched because of the demand for stable lead-free perovskite. Their isolated octahedra making them an ideal playground for studying perovskite structure-property relationships for the A-site cations[1,2]. Recently, tellurium-based double perovskites have been identified as potential lead-free solar cell materials with good electronic attributes and chemical stability[3].

We successfully grew MA_2TeCl_6 single crystals and studied its crystal structure as a function of temperature[4]. Three phases were observed across the temperature range. We report a complete structure solution for each crystallographic phase. Intriguingly, a negative thermal expansion for the *c*-axis in phase II is observed. This is believed to be caused by the different MA^+ ion dynamics in MA_2TeCl_6, compared to the other compounds in the series, such as MA_2SnCl_6[5,6].

The difference of MA_2TeCl_6 drives the necessity to study the phase-transition mechanism and the structure-property relationship. Our structure study is also combined with variable temperature UV-vis spectroscopy to investigate the structure-property relationship for halide perovskite materials. In addition, we have modified the calculation of the Brown radii ratio[7] and extended it to include hybrid A_2BX_6 compounds. Here we demonstrate an improved method to describe the lattice distortion that for ratios between 0.89 and 1.17, where typically the $Fm\bar{3}m$ cubic structure is observed, while mostly distorted structures are found above 1.17.

References

[1] A. E. Maughan, A. M. Ganose, D. O. Scanlon and J. R. Neilson, *Chem. Mater.*, 2019, 31, 1184–1195.

[2] A. E. Maughan, A. M. Ganose, M. A. Almaker, D. O. Scanlon and J. R. Neilson, *Chem. Mater.*, 2018, **30**, 3909–3919.

[3] D. Ju, X. Zheng, J. Yin, Z. Qiu, B. Türedi, X. Liu, Y. Dang, B. Cao, O. F. Mohammed, O. M. Bakr and X. Tao, *ACS Energy Lett.*, 2019, **4**, 228–234.

[4] Y. Liu, J. K. Cockcroft, Z. Chen, M. A. Hayward, P. F. Henry, R. S. Perry and R. G. Palgrave, *J. Mater. Chem. C*, 2022, **10**, 11938–11945.

[5] N. Onoda, T. Matsuo and H. Suga, *Philos. Mag. A*, 1988, **57**, 245–260.

[6] Y. Kume, R. Ikeda and D. Nakamura, *J. Magn. Reson.*, 1979, **33**, 331–344.

[7] I. D. Brown, *Can. J. Chem.*, 1964, **42**, 2758–2767.

The influence of Al and Ga doping on the chemical and electrochemical cycling of T-$LiFeO_2$

Suraj Mahato[1], Xabier Martinez De Irujo Labalde[1], Samuel Booth[2], and Michael Hayward[1]

[1]*Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, OX1 3QR*

[2]*Department of Chemical and Biological Engineering, The University of Sheffield*

Li-ion batteries have transformed our daily life by acting as energy dense, rechargeable power sources for a wide range of electronic devices. Exploration of alternative energy materials are required to satisfy the current and future demands of renewable energy in grid storage and transport industry. Due to limitations on the supply, cobalt and nickel derived cathodes would face problems being applied on a larger scale. To address this challenge, as part of the FutureCat project, we are studying Fe-based cathode materials which could be used for large scale application and it would deliver high energy density owing to Fe^{3+}/Fe^{4+} redox.

Initially, we decided to stabilise the T-$LiFeO_2$ structure by substituting Fe with Al and Ga keeping the atomic arrangements unaltered in the framework. Previously, it was reported that during cycling a structural transformation took place forming the spinel $LiFe_5O_8$ phase, irreversible oxygen loss and capacity fading was also observed [1]. $LiFe_{1-x}M_xO_2$ (M = Al, Ga) samples were prepared and subjected to chemical and electrochemical lithiation, and the effect on the structure, bonding, and oxidation state at various lithium contents was monitored with XRD, SXRD, XANES, titration, and SQUID measurements. The effect of Al and Ga pillaring the T-$LiFeO_2$ structure during the chemical lithium insertion will be discussed in details in the presentation.

References:

[1] A. R. Armstrong et al., J. Am. Chem. Soc. 2008, 130, 3354-3559

[2] Y. Li et al., Nano Energy 47 (2018) 519-526

Scalability of Nb-based Anode Materials

Daniel Martin,[1] Wanwei Zhang[1], Josh Lewis[1], Maurits Houck[1,2], Alex Groombridge[1]

[1] Echion Technologies,

[2] University of Cambridge,

To achieve Net Zero Emissions by 2050, the electrification of large scale hard-to-decarbonise transportation *e.g.,* green rail applications, requires Li-ion batteries with safer characteristics under extreme operating conditions, longer cycle life, lower total cost of ownership, higher energy density and faster charging times. Current commercial anode materials such as graphite, silicon and LTO have typically either high energy density or high power capabilities but lack a combination of both. In the past 15 years, literature has demonstrated that niobium-based Wadsley-Roth crystal structures have high capacity, high Li-ion diffusion rates, and excellent cycle life.[1] These factors, together with the abundancy of niobium, makes them a leading commercial anode material for the next generation of Li-ion batteries used in heavy duty applications.

However, there are several challenges in translating these materials from a lab to an industrial scale, including difficult synthesis methods and harsh engineering conditions. Echion Technologies has developed a variety of niobium-based anode materials via scalable solid-state routes leading to our product XNO®. Here we unveil the journey of optimising XNO® by tuning its physical, chemical, and structural properties. XNO® has been demonstrated in large-format pouch, prismatic and cylindrical cells in combination with numerous cathode materials (up to 400 Wh/L cells showcased, >>10,000 cycles predicted), and will be commercially available at the kT scale in early 2024.

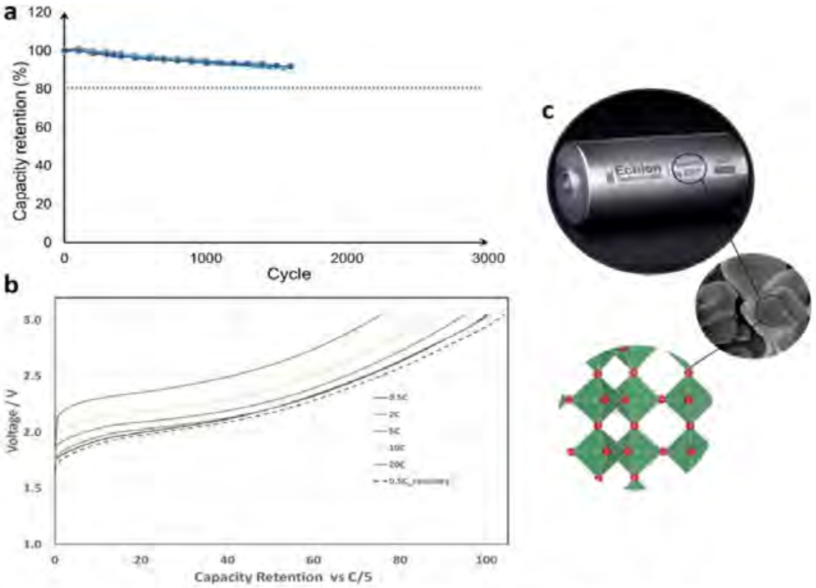


Figure 1: (a) high-loading (20 mg/cm²) cycle life of NCA/XNO® full-cells. (b) charge capability of NCA/XNO® full-cells (7 mg/cm²). (c) Prototype 4690 large-format cell containing micron-sized XNO® anode material.

References

[1] Qinglin Deng, Yanpeng Fu, Changbao Zhu, and Yan Yu, Small, 2019, 15, 1804884.

Ferroelectric and Antiferroelectric Tetragonal Tungsten Bronzes for Ceramic Capacitor Applications

Kerry McMahon[1] and Finlay D. Morrison[1], T. Murata[2], S. Hirose[2], T. Asaka[3] and U. Daisuke[3].
[1] University of St Andrews
[2] Murata Manufacturing Co.
[3] Nagoya Institute of Technology

Multilayer ceramic capacitors (MLCCs) are used in large quantities in every electronic device and current global usage is of the order of 10^{14} parts per annum. With the growing complexity of modern technology, coupled with the drive towards electrification of transportation, the global demand for these devices is currently outstripping available supply and with no sign of slowing.[1] Current MLCCs are based on ferroelectric barium titanate ($BaTiO_3$). However, $BaTiO_3$ exhibits a significant reduction in permittivity above its Curie temperature ($T_C \approx 130$ °C) and under high voltage (field) making it unsuitable for any applications requiring high temperatures and/or fields.[2, 3] Ferroelectric and antiferroelectric tetragonal tungsten bronzes (TTBs), general formula $A1_2A2_4B1_2B2_8O_{30}$, are a potential alternative which are currently being explored. Some TTBs show a temperature stable permittivity and also 'antiferroelectric-like' hysteresis loops and due to their subtle structural distortions, selective doping can be used to manipulate their properties[3-6] to achieve the high technical specifications needed for future devices.

Two TTB families have been explored for these purposes: $Ba_4La_{0.67}\square_{1.33}Nb_{10}O_{30}$ (BLN) and $K_2Pr_{0.75}La_{0.25}Nb_5O_{30}$ (KPLN).[3-5] The structural complexity of these materials require a suite of complementary techniques such as electron, neutron and synchrotron diffraction combined with dielectric, ferroelectric and second harmonic generation measurements in order to disentangle the composition-structure-property interrelationships. Initial results suggest that the complex electrical properties arise from locally competing structures associated with a flat energy landscape.

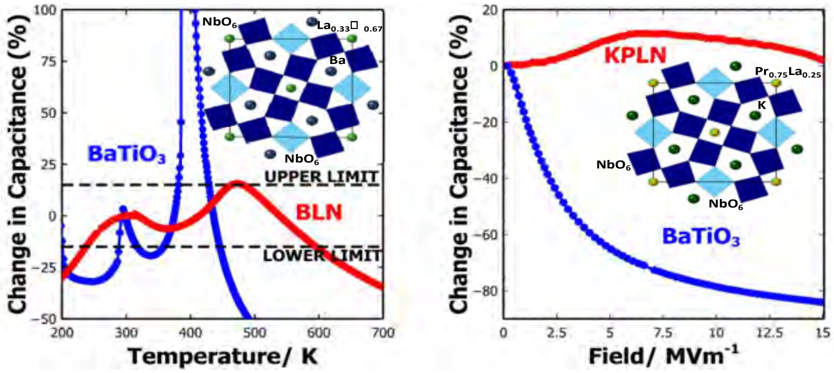


Figure 1 – The % change in capacitance with varying temperature (left) and field (right) of conventional barium titanate (blue) and the potential alternative TTBs (red). Schematics of the corresponding TTB crystal structures are also shown.[5]

References

[1] R.W. Whatmore, Y. You, R. Xiong and C. Eom, *APL Mater.*, 2021, **9**, 1–7.

[2] M.S. Alkathy, R. Gayam and K. J. Raju, *J. Mater. Sci.: Mater. Electron.*, 2017, **28**, 1684–1694.

[3] T. Murata, H. Akamatsu, D. Hirai, F. Oba and S. Hirose, *Phys. Rev. Mater.*, 2020, **4**, 1–11

[4] J. Gardner, F. Yu, C. Tang, W. Kockelmann, W. Zhou and F. D. Morrison, *Chem. Mater.*, 2016, **28**, 4616 – 4627.

[5] J. A. McNulty, D. Pesquera, J. Gardner, A. Rotaru, H. Y. Playford, M. G. Tucker, M. A. Carpenter and F. D. Morrison, *Chem. Mater.*, 2020, **32**, 8492 – 8501.

[6] T. Brown, A. P. Brown, D. A. Hall, T. E. Hooper, Y. Li, S. Micklethwaite, Z. Aslam, S. J. Milne, *J. Eur. Ceram. Soc.*, 2021, **41**, 3416 – 3424.

Exploring the Unusual Magnetic Behaviour of $Mn_2Mo_3O_8$

Holly L. McPhillips,[1,2] Laura J. Vera Stimpson,[3] Gavin B. G. Stenning,[4] Donna C. Arnold[1] and Silvia Ramos.[2]

[1] School of Chemistry and Forensic Science, Division of Natural Sciences, University of Kent, Canterbury, UK, CT2 7NH

[2] School of Physics and Astronomy, Division of Natural Sciences, University of Kent, Canterbury, UK, CT2 7NH

[3] School of Law, Policing and Social Sciences, Canterbury Christ Church University, Canterbury, Kent, UK, CT1 1QU

[4] ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, UK, OX11 0QX

Multiferroic materials that have multiple order parameters co-existing in a single phase and exhibit magnetoelectric (ME) coupling have attracted great interest in the scientific community. For these materials, the magnetic properties and electric polarisation are coupled, resulting in interesting, complex magnetic states with potential applications in areas of quantum computers and spintronics.

The polar hexagonal (S = 5/2) layered oxide $Mn_2Mo_3O_8$ is an example of a material that exhibits large ME coupling that would benefit emerging technological devices. The material crystallises in $P6_3mc$ and is composed of magnetic Mn^{2+} honeycomb sheets, separated by trimerised Mo^{4+} Kagomé-like layers. The magnetic behaviour is driven solely by the honeycomb layer, with little to no contribution from the Mo^{4+} trimers. This results in an easy-axis-type ferrimagnetic ground state below T_c = 41 K[1]. However, a full understanding of the structural and magnetic behaviour of $Mn_2Mo_3O_8$, including when the honeycomb lattice is doped with other 3*d* transition metals, remains limited [2–4].

This discussion will focus primarily on the structure-property correlations within $Mn_2Mo_3O_8$, including the effect of doping with 3*d* transition metals. From these studies, it becomes possible to understand the stability of the magnetic interactions within the honeycomb motif and explore possible geometric magnetic frustration.

References

1 S. P. McAlister, *J. Appl. Phys.*, 1984, **55**, 2343–2345.

2 D. Szaller, K. Szász, S. Bordács, J. Viirok, T. Rõõm, U. Nagel, A. Shuvaev, L. Weymann, A. Pimenov, A. A. Tsirlin, A. Jesche, L. Prodan, V. Tsurkan and I. Kézsmárki, *Phys. Rev. B*, 2020, **102**, 1–8.

3 T. Kurumaji, S. Ishiwata and Y. Tokura, *Phys. Rev. B*, 2017, **95**, 1–9.

4 S. Nakayama, R. Nakamura, M. Akaki, D. Akahoshi and H. Kuwahara, *J. Phys. Soc. Japan*, 2011, **80**, 1–4.

Pushing the Limits of *Operando* X-ray Diffraction and Spectroscopy Studies for Industrial Li-ion batteries

Ashok S. Menon[1], Matthew Capener[1], David Walker[2], Mark Copley[1], and L. F. J. Piper[1]

[1]WMG, University of Warwick, Coventry CV4 7AL, UK
[2]Department of Physics, University of Warwick, Coventry, West Midlands CV4 7AL, UK

Devising practical performance improvement strategies for Li-ion batteries require an in-depth understanding of their degradation during real-world/industrial operation. *Operando* X-ray investigations enable direct correlation of the battery degradation modes to the transient non-equilibrium bulk crystallographic and electronic structure changes in the battery. However, *operando* studies often use cells modified for X-ray transmission that are not representative of real-world long-duration battery operation, thereby compromising the practicality of the results obtained. In this talk, I will present our work on **in-house *operando* X-ray diffraction (XRD) and absorption spectroscopy (XAS) study of industrial single-layer $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$–Graphite A7 full pouch cells which has not been modified for X-ray transmission**. These cells provide stable long-duration (>100 cycles) cycling performance when cycled between high voltages (3–4.4 V) at practical cycling rates. Furthermore, the industry-grade cell manufacturing permits both XRD and XAS studies using the *same* cell, facilitating an accurate correlation of the bulk crystallographic and electronic structure evolution to the electrochemical capacity fade over cycling. As shown in Fig. 1, this methodology allows to correlate the electrochemical capacity loss during prolonged cycling to the evolution of the $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathode and graphite (not shown) structures and the charge compensating Ni-redox activity. This study serves as a benchmark for our own future in-house *operando* studies as well as the wider battery research community.

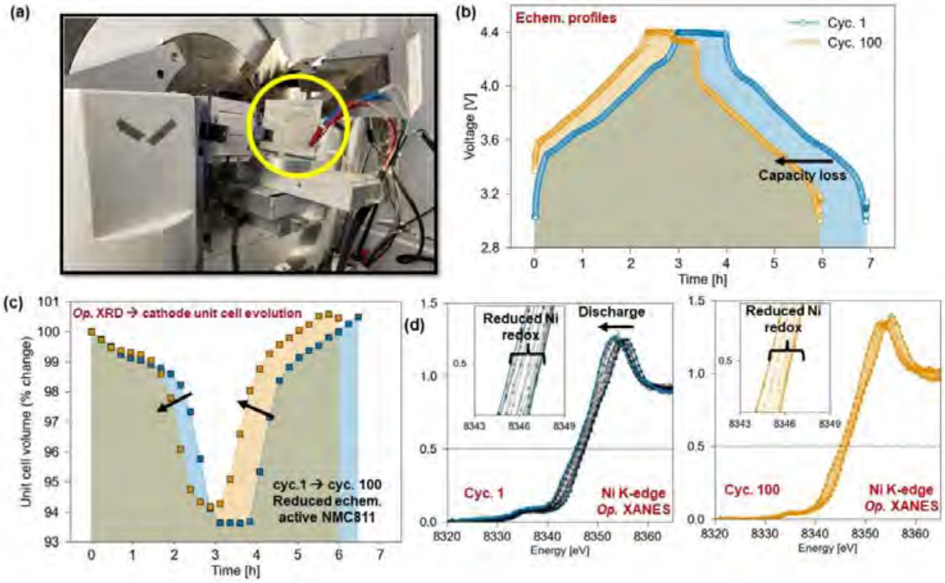


Figure 1: (a) Photograph of the single-layer pouch cell on the diffractometer. (b) Electrochemical (voltage) cycling profiles of the cell during the 1st and 100th cycle. (c) Evolution of the R-3m unit cell volume of the $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathode and (d) the Ni K-edge X-ray absorption near-edge structure spectra (XANES) during those cycles. The changes are highlighted in the figure.

Phase transitions and compositional changes in Ca-Mg-H hydrogen storage systems

Ruby Morris,[1] *and Duncan H. Gregory.*[1]

[1] *School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ.*

The practical use of metal hydrides for hydrogen storage is restricted/dictated by their intrinsic properties. It is therefore vital to understand the relationship between structure and properties for these materials as therein lies the foundation for their development to meet the criteria for hydrogen storage. Ca-Mg-H materials are among the few bimetallic s-block hydrides to show promise as solid-state stores, with attractive gravimetric and volumetric capacity and good cyclability. Therefore, research on these light metal systems is now focused on destabilisation to tackle kinetic / thermodynamic issues of hydrogen release. For ternary systems containing Ca, Mg and H, only two phases have been identified so far: cubic $Ca_{19}Mg_8H_{54}$ and hexagonal $Ca_4Mg_3H_{14}$[1]. Previous syntheses of these compounds have required high pressure hydrogen, but in this work, we describe how both $Ca_{19}Mg_8H_{54}$ and $Ca_4Mg_3H_{14}$ can be synthesised mechanochemically from the binary hydrides without hydrogen gas.

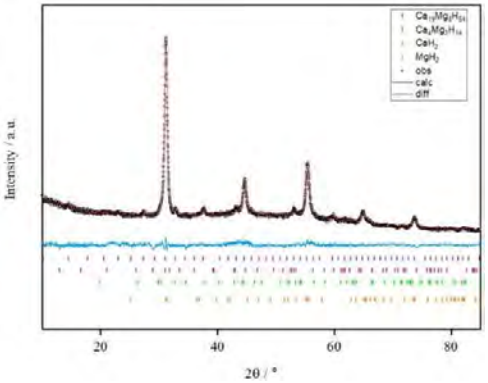


Figure 1: *Refinement profile plot for the 4:3 CaH_2 : MgH_2 sample*

PXD of our mechanochemically-synthesised 4:3 Ca:Mg crystalline sample showed a main ternary phase isostructural to the well-known cubic $Ca_{19}Mg_8H_{54}$[2]. However, research in the group has shown that $Ca_{19}Mg_8H_{54}$ is not a line phase and that the complex cubic structure can tolerate variable metal content.[3] Rietveld refinement against lab PXD data of the 4:3 sample revealed the main cubic phase to have a composition of $Ca_{14.5}Mg_{12.5}H_{54}$, extending the possible stoichiometries of the cubic Ca-Mg-H phase still further.

We seek to arrive at a better understanding of the processes preceding, during and following dehydrogenation so thermogravimetric-differential thermal analysis (TG-DTA) under Ar was followed ex-situ by PXD and Rietveld refinement. Thermal analysis and subsequent structure refinement of the 4:3 sample heated to 225 °C revealed the coexistence of a $Ca_{19}Mg_8H_{54}$-type phase and a hexagonal $Ca_4Mg_3H_{14}$-type phase prior to dehydrogenation. This indicates that the mechanochemically synthesised material first emerges as a cubic phase and then converts to the hexagonal phase at elevated temperatures. It therefore seems increasingly likely that $Ca_4Mg_3H_{14}$ is a metastable hydride. We are investigating the conditions for the formation and growth of this phase and with the aim of testing the flexibility for non-stoichiometry in the hexagonal structure (as we have seen with the $Ca_{19}Mg_8H_{54}$ phase). As we develop a more comprehensive understanding of this system, our strategy will pave the way for methods such as doping, substitution and catalysis towards optimising this material as a reversible solid-state hydrogen store.

References

1. F. Gingl, F.R Bonhomme, K. Yvon, P. Fischer, Tetracalcium trimagnesium tetradecahydride, $Ca_4Mg_3H_{14}$: the first ternary alkaline earth hydride, *J. Alloys Comp., 1992,* ***185****, 273-278.*
2. B. Bertheville, K. Yvon, $Ca_{19}Mg_8H_{54}$, a new salt-like ternary metal hydride, *J. Alloys Comp.*, 1999, **290**, 8-10
3. H. Reardon, *Synthesis, structure, and characterisation of novel lightweight energy materials based on group I & II metal compounds.* PhD thesis, University of Glasgow, 2014.

Quantum Spin Liquids in Cation Ordered Perovskites

Michael J. Milton[1], Pascal Manuel[2], J. Paul Attfield[1]

1. Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Edinburgh EH9 3JZ, UK

2. ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot OX11 0QX, UK

ABO$_3$ perovskites have been a prominent area of research for many years for their ability to incorporate different cation valances and ionic radii. 6H Ba$_3$BRu$_2$O$_9$ perovskites that form a hexagonal $P6_3/mmc$ space group have already been explored for their novel quantum magnetic properties arising from dimer formation. High-pressure high-temperature treatment can be used to induce a transformation to a trigonal P-3m1 (Ba$_3$SrTa$_2$O$_9$ - type) structure[1]. When synthesised using a divalent B cation, the different cation charge and ionic radii of the B site cations can induce cation ordered layers of BO$_6$ and RuO$_6$ dimers in a 1:2 ratio, generating a honeycomb lattice of magnetic cations, often referred to as 3C$_{1:2}$ materials. Currently there is great interest in Ru materials a honeycomb lattice as they are predicted to form a topological quantum spin liquid[2].

We have explored the 3C$_{1:2}$ Ba$_3$BRu$_2$O$_9$ perovskites and successfully synthesised polycrystalline B = Ca and Mg analogues from the corresponding hexagonal precursor. Lab XRD data shows full 1:2 B site ordering of the Ca sample and approximately 5:10 % site disorder with B = Mg sample. The magnetic properties for both samples show very promising quantum spin liquid behaviour, magnetisation shows no magnetic order transitions or hysteresis down to 2K, and an effective paramagnetic moments of around 1.0 μ_B/Ru^{5+}, much reduced from the spin only moment of 3.87μ_B. Heat capacity down to 50 mK further supported the absence of any ordering, and integration of C_{mag}/T shows that the $S = {}^{3}/_{2}$ Ru^{5+} spin entropy for 3C$_{1:2}$-Ba$_3$CaRu$_2$O$_9$ is released up to approximately 80 K, which is in keeping the Weiss temperature of –35 K. Powder neutron diffraction confirmed that there was no long range ordering or structural transitions down to 1.5 K in both samples. The low magnetic moment and apparent dynamic nature of the ground state make these materials promising quantum spin liquid candidates.

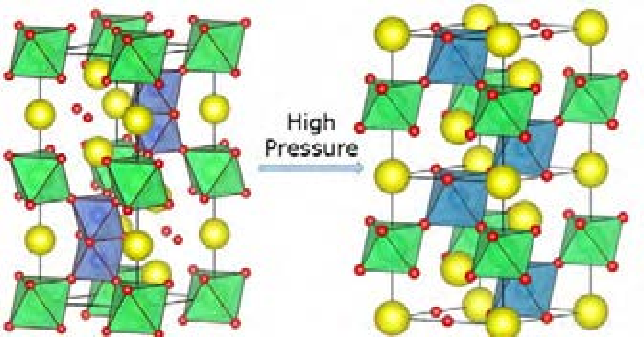


Figure 1: **(left)** Hexagonal perovskite (space group $P6_3/mmc$) **(right)** transformed 3C$_{1:2}$ cation ordered perovskite (space group P-3m1) using high pressure.

References

1) Rijssenbeek, J, T. Saito, T. Malo, S. Azuma, M. Takano, M and Poeppelmeier, R, K. (2005) J. Am. Chem. Soc,127, pg. 675–681.
2) Takagi, H. Takayama, T. Jackeli, G. Khaliullin, G. and Nagler, S. (2019) *Nature Reviews Physics*, 1(4), pg. 264–280.

Dopant Clustering and Vacancy Ordering in Neodymium Doped Ceria

Jing Ming,[1] Marzena Leszczyńska,[2] Marcin Malys,[2] Jan Jamroz,[2] Wojciech Wrobel,[2] Marcin Krynski,[2] Stephen Hull,[3] Franciszek Krok[2] and Isaac Abrahams[1]

[1] Department of Chemistry, Queen Mary University of London, Mile End Road, London E1 4NS, U.K.

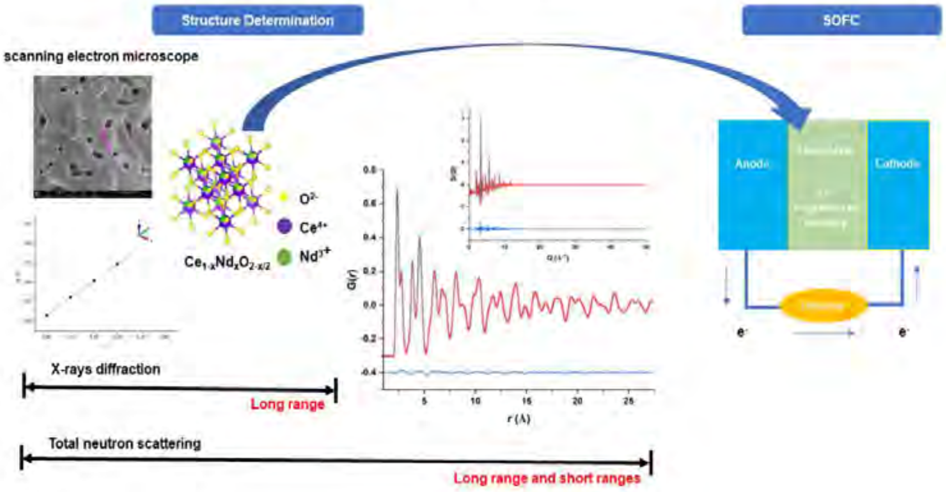
[2] Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland.

[3] STFC ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

Doped cerias with the cubic fluorite structure are used as solid electrolytes for solid oxide fuel cells (SOFCs), especially operating in the intermediate temperature range (600-800 °C).[1] An attractive feature of doping ceria with aliovalent cations is to increase the effectiveness of the materials in application areas by tuning its defect-chemistry. Neodymium doped ceria ($Ce_{1-x}Nd_xO_{2-x/2}$, NDC) is one of these promising materials.[2] Many features in the long-range and macroscopic characteristics of doped cerias have been reported. However, the short range ordering is challenging to determine by conventional average structure methods.[3]

In this study, samples of composition $Ce_{1-x}Nd_xO_{2-x/2}$ ($0.05 \leq x \leq 0.30$) were prepared via solid state reaction. A simple cubic fluorite structure is maintained throughout the studied compositional range. Neutron diffraction reveals oxygen occupancies are fairly close to the theoretical values assuming Ce and Nd to be in the +4 and +3 oxidation states, respectively.

The defect-induced local distortions and short-range correlations in NDC were probed through Reverse Monte Carlo (RMC) modelling of total neutron scattering data. The arrangement of oxygen vacancies in this system have been found to show a preference for the association with Nd^{3+} cations, with these cations clustering to some extent. The vacancy pairs show a non-random distribution.



References

[1] B. C. H. Steele and A. Heinzel, *Nature*, 2001, **414**, 345–352.
[2] D. A. Andersson, S. I. Simak, N. V. Skorodumova, I. A. Abrikosov and B. Johansson, *Proceedings of the National Academy of Sciences*, 2006, **103**, 3518–3521.
[3] A. Borowska-Centkowska, X. Liu, M. Krynski, M. Leszczynska, W. Wrobel, M. Malys, S. Hull, S. T. Norberg, F. Krok and I. Abrahams, *RSC Adv.*, 2019, **9**, 9640–9653.

Jahn-Teller behaviour in a layered nickel oxide with a triangular lattice

Liam A. V. Nagle-Cocco[1], James Steele[1], Camilla Tacconis[1], Joshua D. Bocarsy[1,2], Adam J. Lovett[3], John S. O. Evans[4], Olivier Mathon[5], Joerg Neuefeind[6], Jue Liu[6], Clare P. Grey[2], and Siân E. Dutton.[1]

[1] Department of Physics, University of Cambridge, United Kingdom,
[2] Department of Chemistry, University of Cambridge, United Kingdom,
[3] Department of Materials Science, University of Cambridge, United Kingdom,
[4] Department of Chemistry, Durham University, United Kingdom,
[5] European Synchrotron Radiation Facility, France,
[6] Spallation Neutron Source, Oak Ridge National Laboratory, USA.

$NaNiO_2$ is a layered oxide material consisting of alternating layers of edge-sharing $Ni^{3+}O_6$ and NaO_6 octahedra, with individual cation layers forming a triangular lattice. At high temperatures, its average crystal structure from diffraction is rhombohedral, but cooling below 480 K gives rise to a Jahn-Teller-driven monoclinic distortion in which individual NiO_6 octahedra are all elongated along a parallel axis.

Previous studies on the perovskite-like $LaMnO_3$ [1] have indicated that the Jahn-Teller distortion in this compound persists locally even at temperatures above which the distortion is not present in the average crystal structure (i.e. from diffraction). This is described as an order-disorder transition. There has been recent work speculating on whether there is a similar character to the transition in $NaNiO_2$ [2]. In this work we present the results of neutron Pair Distribution Function and X-ray Absorption Spectroscopy as a function of temperature through the Jahn-Teller suppression, and we elucidate the nature of this transition in $NaNiO_2$ at a local scale. We find that there is no detectable local Jahn-Teller distortion above this temperature, suggesting that the transition has displacive character as opposed to order-disorder.

References

[1] Qiu, Xiangyun, et al. "Orbital correlations in the pseudocubic O and rhombohedral R phases of $LaMnO_3$." Physical Review Letters 94.17 (2005): 177203.

[2] Radin, Maxwell D., John C. Thomas, and Anton Van der Ven. "Order-disorder versus displacive transitions in Jahn-Teller active layered materials." Physical Review Materials 4.4 (2020): 043601.

Synthesis of Layered Lead-Free Materials by Anion Substitution

J. A. Newnham[1], Q. D. Gibson[1], T. W. Surta[1], T. Manning[1], L. Daniels[1], J. B. Claridge[1], and M. J. Rosseinsky[1]

[1] Department of Chemistry, University of Liverpool

Particularly in the areas of photovoltaics, piezoelectrics, and thermoelectrics, there exists a range of high-performance materials that also contain the toxic element, lead.[1-3] Most famously is $MAPbI_3$, which has a photovoltaic conversion efficiency of >20%, but is also toxic and unstable.[1] One potential approach to remove the lead from $MAPbI_3$ is to substitute the Pb(II) for non-toxic Bi(III), and then substitute a single 1- halide for a 2- chalcogenide anion to charge balance. Despite the relative simplicity of this idea, the hypothetical material "$MABiI_2Ch$ (Ch = S, Se, Te)" has not yet been synthesised.[4]

There are however, known materials that could be considered lead-free analogues of each other which utilise this exact approach, for example $BiPbO_2Cl$ and Bi_2O_2Se. With this in mind, we explored a range of other potential new lead-free materials through the substitution of Pb(II) for Bi(III) alongside the diverse range of bonding environments provided by the use of multiple anions.

In doing so, we discover the previously un-reported materials $Bi_8CsO_8SeX_7$ (X = Cl and Br). These layered mixed anion materials have van der Waals gaps and rattling Cs^+ cations resulting in ultra-low thermal conductivities. In this talk, we will discuss how these materials were synthesised and their structures characterised. We will also review their properties and explore some potential applications.

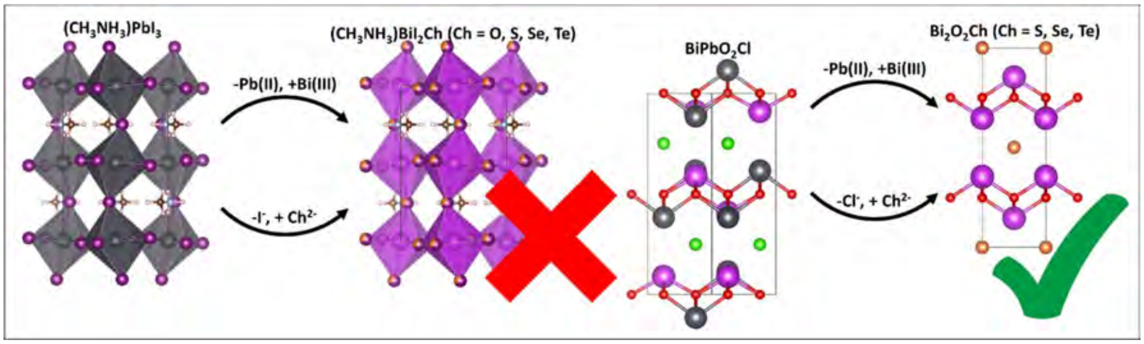


Figure 1: Some materials can be considered Pb-free analogues by simultaneous Pb/Bi and halogen/chalcogenide substitutions, however not all can be synthesised.

References

[1] A. Y. Alsalloum, B. Turedi, X. Zheng, S. Mitra, A. A. Zhumekenov, K. J. Lee, P. Maity, I. Gereige, A. AlSaggaf, I. S. Roqan, O. F. Mohammed, and O. M. Bakr, *ACS Energy Lett.*, 2020, **5**, 657–662.

[2] K. I. Park, J. H. Son, G. T. Hwang, C. K. Jeong, J. Ryu, M. Koo, I. Choi, S. H. Lee, M. Byun, Z. L. Wang and K. J. Lee, *Adv. Mater.*, 2014, **26**, 2514–2520.

[3] Y. Z. Pei, A. LaLonde, S. Iwanaga and G. J. Snyder, *Energy Environ. Sci.*, 2011, **4**, 2085–2089.

[4] F. Hong, B. Saparov, W. Meng, Z. Xiao, D. B. Mitzi and Y. Yan, *J. Phys. Chem. C*, 2016, **120**, 6435–6441

Investigating the impact of intrinsic defects on Cu2SiSe3 for PV applications

Adair Nicolson,[1,2] Seán R. Kavanagh,[1,2,3] Graeme W. Watson,[4]
and David O. Scanlon[1,2]

[1]Thomas Young Centre and Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

[2]Department of Chemistry, University College London, London WC1H 0AJ, U.K.

[3]Thomas Young Centre and Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, U.K.

[4]School of Chemistry and CRANN, Trinity College Dublin, College Green, Dublin 2, Ireland

Metal chalcogenides have seen renewed interest in recent years with the hope that they will deliver stable, non-toxic thin-film solar cells with efficiencies that can match silicon and halide perovskite-based devices.[1] To this end we have begun an initial investigation into the electronic and optical properties of Cu_2SiSe_3, and it has shown initial promise as a photovoltaic absorber with a calculated band gap of ~1.52 eV and a maximum efficiency of 30% for a 1.5 mm film.

However, a promising band gap and absorption coefficient is not sufficient to determine if a new material will achieve high efficiencies in devices. Non-radiative recombination processes, driven by defect states in the band gap, can drastically reduce carrier lifetimes, and thus performance.[2] Therefore, in this project we investigate all potential intrinsic defects in Cu2SiSe3 to determine how they may affect carrier lifetimes and thus device performance.

References

1 Hadke, S.; Huang, M.; Chen, C.; Tay, Y. F.; Chen, S.; Tang, J.; Wong, L., Chem. Rev., 2021.

2 Huang, Y.-T.; Kavanagh, S. R.; Scanlon, D. O.; Walsh, A.; Hoye, R. L. Z. Nanotechnology, 2021, 32 (13), 132004.

Modelling Niobium based Solid Electrolytes for Lithium-ion Batteries

Bassey Oboho[1]

[1] Loughborough University

In an effort to create an all-solid state lithium-ion battery, a Niobium based gar- net material ($Li_5La_3Nb_2O_{12}$, LLNO) is a promising alternative to the common Zirconium based solid electrolyte. Niobium normally exhibits oxidation states ranging from +3 to +5. This virtue alone makes Niobium a challenging element to model theoretically as a main component element or as a main doping element.

There are a few papers that experimentally introduce LLNO as a viable solid electrolyte and shows that the addition of external defects improves the energy density and electrochemical performance of the battery. However, it is shown that the unit cell of LLNO varies depending on the preparation technique and the type of external defect used; making this a controversial material. To this day there are no modelling papers on a pure LLNO material.

In this talk, I will show theoretically that pure LLNO adopts a cubic crystal system of around 12.75 ̊A supported by Bo et al.[1]. I will also show that using Zinc and Titanium as a dopants is more favourable on the Niobium site than on the Lanthanum site but still maintains its cubic crystal system.

References

[1] B. Dong, M. Stockham, P. Chater, and P. Slater, “X-ray pair distribution function analysis and electrical and electrochemical properties of cerium doped li 5la 3nb 2o 12garnet solid-state electrolyte,” Dalton Transactions, vol. 49, pp. 11727–11735, Sept. 2020.

Material design of quaternary sodium halide electrolytes

Anthony Onwuli,[1] Alex Ganose,[2] Aron Walsh,[1,3] Ainara Aguadero,[1,4] and Ieuan Seymour.[1]

[1] Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK,

[2] Department of Chemistry, Imperial College London, White City Campus, London W12 0BZ, UK,

[3] Department of Physics, Ewha Womans University, Seoul 03760, Korea,

[4] Instituto de Ciencia de Materials de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain

The future of electrochemical energy storage can be considered to be within the development of all-solid-state batteries (ASSBs). The key to enabling this future resides in the development of solid-state electrolytes (SSEs). For lithium-ion battery systems, halide electrolytes have been reported with room temperature ionic conductivities >10^{-3} S cm^{-1}, good stability against oxidation, and good stability against cathode materials[1]. We find that the space explored for sodium halide electrolytes has been rather limited within the literature and primarily focused on ternary sodium chloride SSEs with limited investigation of sodium bromide and iodide SSEs[2,3,4]. Previous studies have demonstrated that Li-halide systems such as Li3YCl6 (P-3m1) and Li3InCl6 (C2/m) form layered structures with high ionic conductivity, whereas ternary halides such as Na3YCl6 often form double perovskite structures (P21/n) with intrinsically low ionic conductivity. Discovering new layered Na-halide systems is crucial to improving this ionic conductivity of this class of materials. This study provides a high-throughput materials design workflow to provide insight into the development of quaternary sodium metal halide SSEs through theoretical calculations of thermodynamic stability, electrochemical stability, stability against common sodium cathodes, transport properties as well as synthesis of $Na_6M'M''X_{12}$ SSEs. 3710 compositions are considered in four different space groups, P21/n, P-3m1, P31c, C2/m. Our candidate pool is screened to 25 candidates by filtering for a ground state phase in the C2/m structure, on the convex hull ($E_{hull}=0$), no radioactive elements and an insulator (PBEsol bandgap >2 eV). High oxidation potentials are often observed for the candidates indicating stability against cathodes. Further interface thermodynamics stability analysis revealed that there is a driving force for reactions at the interface between the SSEs and cathodes. On-the-fly machine learning molecular dynamics (MLMD) was used to probe the ionic conductivity of the candidates. Synthesis of promising candidate material Na6CaZrBr12 revealed the existence of a sodium halospinel phase not initially considered in the initial high-throughput screening. The high-throughput screening and synthesis performed in this study can provide design principles for the development of new SSEs and can be extrapolated to other conducting-ion systems as well as providing a method to expand the search space of known SSE chemistries.

References

[1] Hiram Kwak et al., *ACS Energy Letters*. 2022, **7**, 1776-1805

[2] Dongsu Park et al., *Journal of Materials Chemistry A*, 2021, **9**, 23037-23045

[3] Erik A. Wuet al., *Nature Communications*, 2021, **12**, 1256

[4] Yu Qie et al., *The Journal of Physical Chemistry Letters*, 2020, **11**, 3376−3383

Characterisation of Ceria and Ceria-Zirconia Materials Using Advanced Analytical Techniques

Jacob A Oyarzabal,[1] Loredana Mantarosie,[2] David Thomsett,[2]
Martin R Lees[3] and Richard I Walton.[1]

[1]Department of Chemistry, University of Warwick, CV4 7AL, United Kingdom,

[2] Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading, RG4 9NH,

[3] Department of Physics, University of Warwick, CV4 7AL, United Kingdom

Given the effect greenhouse gases have on our climate which are fuelling the current climate crisis, methods of reducing greenhouse gas emissions are of key importance. The use of heterogeneous catalysts is one such method, utilised in a wide array of different settings, all with the aim of turning harmful gases into something less polluting. One of the most commonly used, and industrially relevant, of these materials are ceria and ceria-based materials. The redox chemistry of cerium allows these materials to be used for oxygen storage in applications such as the three-way catalytic converter, which help to reduce emissions from vehicles.[1]

The aim of this project is to use probes of paramagnetism in the solid state to characterise heterogeneous catalysts: this will include magnetic measurements with variable field and temperature, and electron spin resonance spectroscopy. The results will be combined with data from diffraction and X-ray spectroscopy to gain new insights into the local structures of industrially relevant catalysts.

By use of SQUID magnetometry it has been shown that, as expected, the ceria and ceria-zirconia materials are largely diamagnetic, however at low temperatures a Curie-Weiss-like tail is observed. This is indicative of a small amount of paramagnetism within the sample, which has been shown by EPR spectroscopy. This is interpreted as being due to small concentrations of cerium(III) within the materials, which are at too low a level to be seen by cerium L_{III}-edge XANES spectroscopy. Cerium K-edge EXAFS has been used to investigate the local structure of these ceria and ceria-zirconia materials to examine the possibility of local ordering of Ce and Zr in the ternary materials.

References

[1] T. Montini, M. Melchionna, M. Monai, P. Fornasiero, *Chemical Reviews*, 2016, **116**, 5987-6041

[2] K. Ackland, J.M.D. Coey, *Physics Reports*, 2018, **746**, 1-39

Atomic Layer *vs.* Sol-Gel Deposited Coatings for Long Cycle-Life Li-ion Battery Cathodes

Rory Powell,[1,2] Jungwoo Lim,[1,2] Alex R. Neale,[1] Adrian Gardner,[1] Paul Chalker,[3]
Laurence J. Hardwick[1, 2]
[1]Stephenson Institute for Renewable Energy, University of Liverpool, Peach St,
Liverpool, L69 7ZF
[2]The Faraday Institution, Quad One Becquerel Avenue Harwell, Didcot, OX11 0RA
[3]Department of Mechanical, Materials & Aerospace Engineering, George Holt
Building, University of Liverpool, Brownlow Street, Liverpool, L89 3GQ

High nickel content layered oxide cathodes for Li-ion batteries suffer from capacity fade due to, among other factors, particle cracking induced by lithiation/delithiation, transition metal dissolution into the electrolyte, and attack from HF. Surface modification has been shown to reduce the severity of these degradation mechanisms by blocking transition metal ions from dissolving, and protecting the surface from the electrolyte decomposition products, as well as physically restraining the particles to reduce cracking. Atomic layer deposition (ALD) is a coating method that promises good uniformity and a high level of thickness control with a wide range of possible coating materials. ALD is a derivation of chemical vapor deposition in which chemical precursors are injected separately into a low pressure heated reaction vessel. The reaction steps are self-limiting, allowing monolayers of precursor to be deposited on each cycle.[1] This coating method offers potential advantages compared to conventional coating methods such as sol-gel.

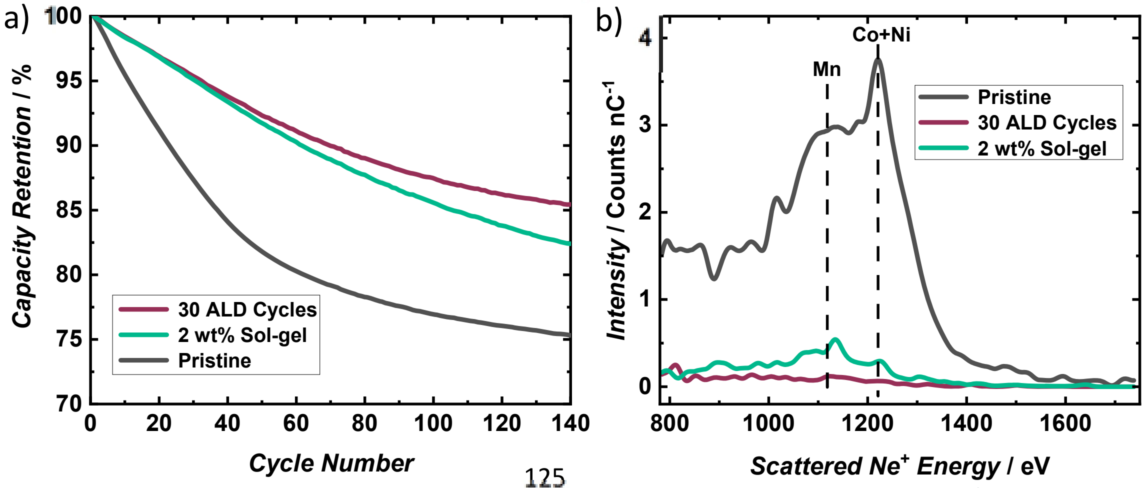
Alumina, Al_2O_3, being the archetypal ALD coating material has been frequently explored to improve the stability of known Li-ion positive electrode materials.[2] Recently Wang *et al.* found marked stability improvement of Al_2O_3 coated $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ over even as few as 40 charge/discharge cycles.[3]

In this work, we present a comparison study of alumina coatings on $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ deposited by ALD versus coatings prepared through a sol-gel method tested to 4.5 V *vs.* Li^+/Li. Depositing a range of Al_2O_3 thicknesses by ALD we see a general trend of increased capacity retention with increased coating thickness. Multiple Al-containing precursors have been investigated for sol-gel coatings and we have found varying results, some giving comparable performances to the ALD coated samples, with others resulting in poorer performance than the uncoated material. Both types of films have been characterised by low energy ion scattering to detect the presence of the coatings, as well as electron microscopy with energy dispersive x-ray spectroscopy to characterise the uniformity and thickness of the coatings.

[1] R. L. Puurunen, *J. Appl. Phys.*, 2005, **97**, 121301.

[2] L. A. Riley, S. V. Atta, A. S. Cavanagh, Y. Yan, S. M. George, P. Liu, A. C. Dillon, and S. Lee, *J. Power Sources*, 2011, **196**, 3317–3324.

[3] X. Wang J. Cai, Y. Liu, X. Han, Y. Ren, J. Li, Y. Liu, and X. Meng, *Nanotechnology*, 2020, **32**, 115401.



a) Capacity retention of pristine and coated samples at 1C and 2.5-4.5 V vs. Li^+/Li, b) Ne^+ LEIS spectrum of pristine (grey), ALD coated (red), and sol-gel coated (green) powders.

The crystallisation and characterisation of basic magnesium chloride salts studied *in situ* using a laboratory SAXS/WAXS instrument.

Katie Pickering,[1] Steven Huband,[2] Kirill Shafran[3] and Richard Walton.[1]

[1] Department of Chemistry, University of Warwick, Coventry.

[2] X-Ray Research Technology Platform, Department of Physics, University of Warwick, Coventry.

[3]BYK Additives Ltd., Moorfield Road, Widnes.

We demonstrate a method for monitoring the *in situ* crystallisation of basic magnesium chloride salts $Mg_{x+y}(OH)_{2x}Cl_{2y}\cdot zH_2O$ using a laboratory based SAXS/WAXS instrument. Although laboratory-based SAXS/WAXS instruments have limitations compared to synchrotron based sources, we have demonstrated how they can provide new insights into the formation of these materials.[1]

The salts were synthesised using a mixture of $MgCl_2$ aqueous solution and nano-sized MgO. The reagent mixture was transferred to a disc-shaped reaction cell, consisting of a circular metal washer with internal diameter of 4 mm and thickness 0.5 mm sealed, each side using Kapton® tape. Although the synthesis of basic magnesium chloride salts has been reported,[2-3] by monitoring their synthesis using simultaneous SAXS and WAXS we are able to obtain time resolved data showing the phase evolution of the material and particle size.

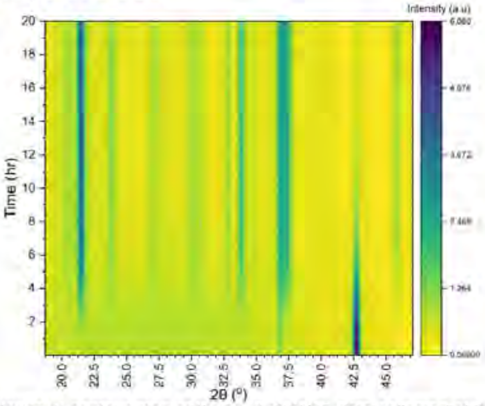


Figure 1: *contour map of the in situ WAXS data collected at 28 °C.*

Using the *in situ* WAXS data, ***Figure 1***, a two-phase Rietveld refinement was carried out to quantify the progress of the reaction over time. The extracted phase fraction allows the decay of the MgO starting material and growth of product phase(s) to be observed directly over a period of several hours. Avrami kinetics were fitted to the data from which we suggest that there are two competing mechanistic processes in the formation of $Mg_3Cl(OH)_5\cdot 4H_2O$. This was then compared to the SAXS data, analysed using combined sphere and Porod gradient model. With SAXS being sensitive to particle size below 160 nm, we observe a reduction in the volume fraction of the primary MgO particles during the initial stages of the reaction and, at later stages of the reaction, the emergence of larger crystalline material. Considering the SAXS and WAXS data we observed an offset between the consumption of crystalline MgO in the WAXS and reduction in the sphere volume fraction in the SAXS. We suggest this is due to the formation of an amorphous $Mg(OH)_2$ intermediate during the synthesis of $Mg_3Cl(OH)_5\cdot 4H_2O$. In conclusion, by simultaneous acquisition of both SAXS and WAXS, new mechanistic insights and quantitative kinetic information has been obtained for the formation of basic magnesium chloride salts.

References

[1] K. S. Pickering, S. Huband, K. L. Shafran, R. I. Walton, *Chemistry–Methods,* 2022, **2**, 9.

[2] A. N. Christensen, P. Norby and J. C. Hanson, *J. Solid State Chem.*, 1995, **114**, 556–559.

[3] A. N. Christensen, P. Norby and J. C. Hanson, *Acta Chem. Scand.*, 1995, **49**, 331–334.

Design Principles for Grain Boundaries in Solid-State Lithium-Ion Conductors

James Quirk and James Dawson
[1] School of Natural and Environmental Sciences, Newcastle University,
Newcastle Upon Tyne, NE1 7RU, UK

Solid-state lithium-ion batteries promise high energy densities and excellent safety, but there are many challenges to overcome before these goals can be realised. Crucial to the operation of solid-state batteries is the solid electrolyte, which must be able to compete with more traditional liquid electrolytes. Solid electrolytes are typically produced through the sintering of powders, meaning that grain boundaries are highly prevalent and should be expected to have profound effects on the performance of a device across its lifetime. These effects might include a reduction in efficiency through decreased ionic conductivity, or even device failure through encouraging the formation of dendrites. Experimental studies on polycrystalline materials are notoriously difficult to perform and interpret, so computational techniques are invaluable for providing insight at the atomic scale.

We carry out first-principles calculations on grain boundaries in four archetypal examples of materials in different classes of solid electrolytes, namely, an oxide antiperovskite (Li_3OCl) and its hydroxide counterpart (Li_2OHCl), a polyanionic sulfide (Li_3PS_4) and a distorted rock-salt halide (Li_3InCl_6). By performing ab-initio molecular dynamics on the bulk and grain boundaries of each material, we demonstrate the differing impacts that grain boundaries have on ionic mobility in each class of material. Even where grain boundaries do not significantly impact ionic conductivity, we consider to what degree perturbations to the electronic structure, such as narrowed band gaps and the presence of charge traps, should be expected to contribute to undesirable electrical conductivity and to dendrite formation. These results highlight important aspects of grain boundaries that must be considered when engineering solid electrolyte materials.

Structure and conductivity of $LiTa_2PO_8$ solid state electrolyte

Peng Ren,[1] Isaac Abrahams[1] and Konrad Kwatek.[2]

[1] Department of Chemistry, Queen Mary University of London, Mile End Road,
London E1 4NS, UK,

[2] Faculty of Physics Warsaw University of Technology, Koszykowa 75, 00-662
Warsaw, Poland.

A new lithium ion conductor $LiTa_2PO_8$ (LTPO) was synthesized in 2018.[1] LTPO shows excellent ionic conductivity ($\sigma_{bulk} = 1.6 \times 10^{-3}$ S cm^{-1}, $\sigma_{total} = 2.5 \times 10^{-4}$ S cm^{-1}) at room temperature.[1] The promising conductivity relates to the crystal structure of LTPO. In the structure, three distinct Ta atoms are located in octahedral sites. There is one crytallographically distinct P atom forming a PO_4 tetrahedron. The TaO_6 and PO_4 polyhedra form a 3D framework, with Li ions disordered over 3 cryatallographic sites. According to Kim et al,[1] a 3D pathway generated by the polyhedra may make Li ions move more easily resulting in high conductivity. According to DFT calculations and AIMI simulations by Hussain et al,[2] the diffusion activation energy is only 0.16 eV. With a quasi-two-dimensional (2D) honeycomb Li diffusion network, the intrinsic ionic conductivity of LTPO is predicted to be up to 35.3 mS/cm at room temperature. That result is quite far from the experimental data. Besides improving the sintering process, more details on the local structure are needed.

MAS-NMR characterization was carried out to study the phosphorous environment. Fig. 1a shows the ^{31}P MAS-NMR spectrum and reveals a complex set of resonances. Modelling of the centre band resonances shows a diverse set the chemical environment confirming that the local structure of LTPO is more complex than the spatially averaged picture derived from the X-ray and neutron diffraction.

The Nb-doped LTPO samples have also been prepared and characterised. While the structure of Nb-doped LTPO is indistinguishable from that of the unsubstituted system, the ^{31}P MAS-NMR spectrum of Nb-LTPO looks quite different from that of pure LTPO. The centre band region is much simpler suggesting the phosphorous environment is more ordered. Impedance spectroscopy confirms that the conductivity of Nb-doped LTPO is equally high as in the parent LTPO.

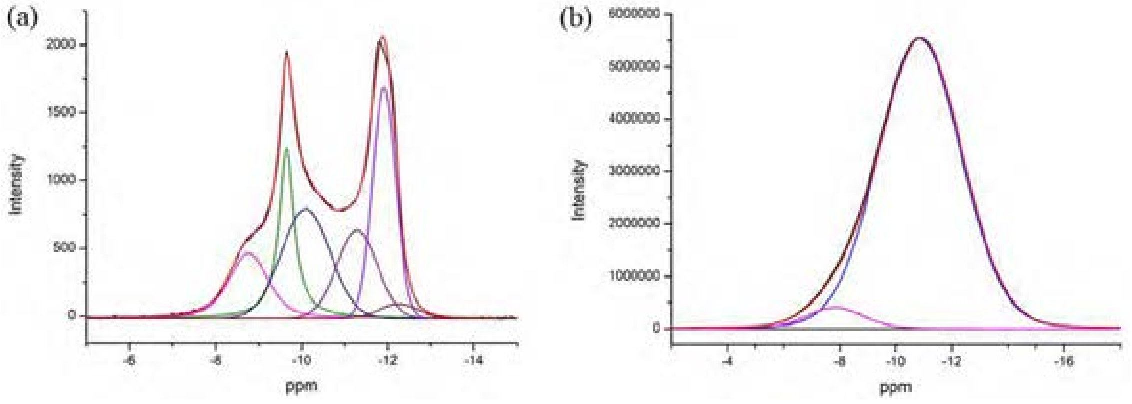


Fig 1 ^{31}P MAS-NMR spectra of (a) LTPO and (b) Nb doped LTPO

References

1 J. Kim, J. Kim, M. Avdeev, H. Yun and S. J. Kim, *J Mater Chem A*, 2018, **6**, 22478–22482.
2 F. Hussain, P. Li and Z. Li, *J. Phys. Chem. C*, 2019, **123**, 19282–19287.

Probing Ion Mobility in Fluorine-Doped Anti-Perovskite Solid Electrolytes

George E. Rudman,[1,2] Euan J. Singleton,[1] Kunj Kapur,[1] James A. Dawson[2] and Karen E. Johnston.[1]

[1] Department of Chemistry, Durham University, Durham, UK,

[2] Chemistry, School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, UK.

All-solid-state batteries are widely regarded as a potential mechanism for delivering future improvements in both the performance and safety of batteries. Current commercial Li-ion batteries use flammable organic liquid electrolytes, which pose significant safety risks owing to potential electrolyte leakage. In contrast, solid-state batteries, i.e., those employing a solid electrolyte material, are less likely to explode or ignite if the battery is damaged. In addition, solid electrolyte materials can offer improvements in cost, energy density, long-term stability and ionic conductivity, enabling less expensive and more efficient batteries with longer life spans to be produced. One particularly promising class of solid electrolyte materials are lithium-rich anti-perovskites (LiRAPs), such as Li_3OCl, which have both good ionic conductivity and interfacial stability.[1] Recent studies have shown that doping LiRAPs can potentially stabilise a room temperature cubic phase, leading to increased ionic conductivities at room temperature.[2] In addition, recent work suggests that lowering the dimensionality of the connected octahedra of the anti-perovskite can potentially lead to lower Li ion migration barriers, resulting in superionic conductivity, i.e, ionic conductivity above 1 mS cm^{-1}, at room temperature.[3]

A series of fluorine-doped LiRAPs, $Li_2OH_{(1-x)}F_xCl$, $Li_2OH_{(1-x)}F_xBr$ and $Li_2OH_{(1-x)}F_xCl_{0.5}Br_{0.5}$ ($x = 0 - 0.9$) have been synthesised using two different air-sensitive solid-state methods and their atomic-level structure has been characterised using multinuclear (^{1}H, ^{7}Li, ^{19}F, ^{35}Cl and ^{79}Br) solid-state NMR spectroscopy. Complementary molecular dynamics simulations have been carried out for a range of hypothetical low-dimensional networked fluorine-doped LiRAPs in order to gain further structural insight and understanding. Our current understanding of the structure and ionic conductivity in fluorine-doped LiRAPs will be presented and discussed.

References

[1] J. A. Dawson, T. Famprikis and K. E. Johnston, *J. Mater. Chem. A*, 2021, **9**, 18746-18772.

[2] Y. Li, W. Zhou, S. Xin, S. Li, J. Zhu, X. Lü, Z. Cui, Q. Jia, J. Zhou, Y. Zhao and J. B. Goodenough, *Angew. Chem. Int. Ed.*, 2016, **55**, 9965-9968.

[3] Z. Lu, J. Liu and F. Ciucci, *Energy Storage Materials*, **28**, 2020,146-152.

A Computational Re-evaluation of Se as a Solar Absorber

Alp E. Samli,[1] Seán R. Kavanagh[1,2] and David O. Scanlon.[1]

[1] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ,*

[2] *Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ.*

Trigonal selenium (c-Se) was the first material to exhibit the photovoltaic (PV) effect and has recently experience a renaissance in research interest due to its desirable properties (suitable band gap, high earth abundance, low temperature processing and 'simple' chemistry) and potential implementation in silicon tandem cells.[1] Though cell efficiencies have improved much since 1883, c-Se lags behind leading technologies such as silicon and lead-halide perovskites.[2]

In this work, we use hybrid density functional theory (DFT) to investigate crystalline selenium's 5 known synthesisable polymorphs (trigonal, rhombohedral, β-monoclinic, γ-monoclinic, δ-monoclinic) and determine the ideal phase for solar cell operation. Trigonal Se has the lowest direct band gap (1.904 eV with spin-orbit coupling) and highest charge carrier mobilities, allowing it to reach the highest efficiencies. Analysis of the optical response shows that c-Se has a theoretical upper limit to its efficiency as a single-junction solar absorber of 23% at a thickness of 2 μm. We calculate the vacuum alignment of the electronic band edges, providing guidance for further optimisation of the absorber contact layers. In addition, we compute the formation energies and charge transition levels of all intrinsic point defects (vacancies and interstitials) at the hybrid DFT level, to characterise the defect chemistry and doping response in this material.

References

[1] M. Zhu, G. Niu and J. Tang, *J. Mater. Chem. C*, 2019, **7**, 2199–2206.

[2] T. K. Todorov, S. Singh, D. M. Bishop, O. Gunawan, Y. S. Lee, T. S. Gershon, K. W. Brew, P. D. Antunez and R. Haight, *Nat. Commun.*, 2017, **8**, 682.

Pitfalls in cation and anion mutation of quaternary chalcogenide semiconductors

Susan Schorr,[1,2] David Matzdorff[1,2] and Galina Gurieva.[3]
[1]Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, 14109 Berlin,
[2]Freie Universität Berlin, Malteserstr. 74-100, 12249 Berlin.

Most of the current commercial photovoltaic devices are exclusively formed by a single junction solar cells, independently on the used technology. This device configuration allows to achieve a maximum theoretical efficiency in the range of 30-33% depending on the used absorber material with an optimal band gap energy of 1.3 – 1.4 eV[1,2]. To achieve further cost reductions in thin film solar cell technologies, devise efficiencies must be increased beyond the single-junction limit. Therefore, there is an increasing interest in semiconductor materials which are potentially suitable for an application as absorber layer in the top cell of a tandem device with e. g. a silicon-based solar cell bottom cell. This requires from the top cell absorber a wider band gap in the range of 1.7 eV. Furthermore, these absorber materials should have a high absorption coefficient for solar light and should contain only earth abundant and non-toxic elements.

Quaternary chalcogenide semiconductors, like Cu_2ZnSnS_4, Cu_2ZnGeS_4, $Cu_2ZnGeSe_4$ or $Cu_2ZnSiSe_4$ show high absorption coefficients, contain only earth abundant, non-toxic elements and have band gap energies between 1.4 eV and 2.2 eV. In order to achieve absorber materials with the required band gap energy of 1.7 eV, cation and anion mutation is an established method for flexible band gap energy tuning.

The formation of solid solution series of $Cu_2B^{II}C^{IV}X_4^{IV}$ compound semiconductors (*B*=Mn, Zn *C*=Si, Ge, Sn and *X*=S, Se) achieved by alloying (mutation) of cations and anions, poses some difficulties in case the end members of the series crystallize in different crystal structure types[3]. There are four different structure types possible: the stannite, the kesterite, the wurtz-stannite and the wurtz-kesterite structure, all based on corner sharing tetrahedra. Comparing these crystal structure types, the network of corner sharing tetrahedra is preserved but the symmetry decreases by tilting of the coordination polyhedra as well as shifting the cations and anions to more general positions.

We performed a comprehensive study of solid solution series based on $Cu_2B^{II}C^{IV}X_4^{IV}$ compounds to tune the band gap energy of the material to an optimal value. We have synthesized powder samples by solid state reaction and investigated the crystal structure of the mixed crystals by a combination of X-ray and neutron diffraction as well as Multiple Edge Anomalous Diffraction (MEAD)[4].

We can show that the transformation from the stannite to the kesterite type structure within a solid solution series is characterized by a cation re-distribution process. Thus, by tuning the band gap energy to the optimal value by alloying, the structural disorder in the material increases which might have negative influences on the solar cell efficiency. In case the end members crystallize in the kesterite and the wurtz-kesterite type structure a 2-phase region exists where two chemical identical mixed crystals but with different crystal structures coexist. Such compositional regions should be avoided in the application as absorber material, because these two phases will have different band gap energies which is detrimental for the solar cell efficiency.

Carefull investigations of the crystal structure of the mixed crystals of a solid solutions series can avoid pitfalls of having a compound semiconductor with the optimal band gap energy value but exhibit properties detrimental for a solar cell application.

References

[1]W. Shockley, H. J. Queisser, *Journal of Applied Physics, 1961,* **32**, 510–519.

[2]S. Rühle, *Solar Energy,* 2016, **130**, 139-147.

[3]S. Schorr, *Solar Energy Materials and Solar Cells,* 2022*,* **249**, 112044.

[4]D. M. Többens et al., *Acta Crystallographica B,* 2020*,* **76**, 1027-1035.

Discovery and property investigation of new intermetallic compounds

Katie C. Scott[1], Quinn D. Gibson[1], Michael W. Gaultois[1], Luke M. Daniels[1], Jonathan Alaria[2] and Matthew J. Rosseinsky[1]
[1]*Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD*
[2]*Department of Physics, University of Liverpool, Oxford Street, Liverpool, L69 7ZE*

Intermetallics and toplogical materials are known to exhibit exotic properties like magnetism and superconductivity resulting from the interaction between crystal structure, magnetic structure and conduction electrons. By targeting the synthesis of new intermetallic materials, investigation of new quantum phenomena (such as Weyl semimetals, chiral metals or topological insulators) is possible which further enhances our understanding of fundamental chemistry and physics. Intermetallics also have wider industrial applications, some examples being low energy IT systems, electric generators and as permanent magnets used in the motor industry.

In order to study these materials and their complex properties we need to grow and analyse suitable single crystals. Novel intermetallics are usually made of high melting point metals which require arc welding, high furnace temperatures and repeated grindings for synthesis. These are not ideal conditions for single crystal growth. We utilise low melting point metals that act as a solvent along with slow cooling in order to grow large enough crystals for measurements.[1,2]

Here we present the structure, synthesis and physical properties of two novel intermetallic compounds in the Hf-M-Sn phase field (M = transition metal). The crystal structures of these new materials were unambiguously determined by single crystal X-ray diffraction and are analogous to the previously reported $Hf_9Fe_4Sn_{10}$ single crystal phase.[3] Detailed magnetic studies along with electron transport properties are presented, giving us a broad understanding of these novel materials.

1 M. G. Kanatzidis et al., *Angew. Chemie - Int. Ed.*, 2005, **44**, 6996–7023.
2 W. A. Phelan et al., *Chem. Mater.*, 2012, **24**, 409–420.
3 N. P. Calta et al., *J. Solid State Chem.*, 2016, **236**, 130–137.

Searching for magnetoelectric coupling in the new cubic perovskite $CeBaMn_2O_6$

S. Simpson,[1] J. P. Tidey[1], F. Pomiro[1], W. Chen[2], and Mark Senn[1]
[1] Department of Chemistry, University of Warwick, Gibbet Hill, Coventry, CV4 7AL, U.K.
[2] Center for Condensed Matter Sciences, National Taiwan University, Roosevelt Road, Taipei 10617, Taiwan.

Transition metal oxides based on the ABX_3 perovskite structure are well known for their exotic magnetic and electronic properties. Prominent examples include colossal magnetoresistance in $Ln_{1-x}A_x\mathrm{MnO_3}$ (Ln = lanthanide, A = divalent metal) [1] and multiferroicity in $TbMnO_3$ [2]. Such properties can arise in perovskite oxides as a direct consequence of the strong coupling between their lattice, magnetic, and electronic degrees of freedom, hence it is of wider interest to elucidate how this coupling may be exploited to engineer desirable properties into perovskite architectures.

Recently, we have developed a group-theoretical approach to enumerating mechanisms of magnetoelectric coupling in perovskite materials [3]. The approach parameterises degrees of freedom within the perovskite structure in terms of symmetry-adapted irreducible representations (irreps) of the cubic $Pm\bar{3}m$ aristotype. In this way, magnetoelectric coupling can be mapped on to the search for specific combinations of orderings transforming as irreps that can be engineered into a given structure. Based on this approach, we have identified the new perovskite composition $CeBaMn_2O_6$ as a promising prototype. This composition should possess the necessary combination of irreps to exhibit multiferroic order, namely: layered cation order on the *A* site; *Pnma*-like MnO_6 octahedral tilting (Glazer notation: $a^-b^+a^-$); and A-type antiferromagnetic order on the Mn site.

Using high-pressure synthesis conditions, we have prepared $CeBaMn_2O_6$ for the first time. Surprisingly, Rietveld fits against high-resolution X-ray and powder neutron diffraction (PND) data show that, despite its low tolerance factor ($t = 0.96$), $CeBaMn_2O_6$ retains $Pm\bar{3}m$ symmetry (**Fig. 1a**) upon cooling to 1.5 K. Large anisotropic displacement parameters on the O site at 1.5 K suggest there is some static tilting of the MnO_6 octahedra. Upon cooling to 1.5 K, diffuse scattering emerges at approximately twice the cubic lattice parameter ($d \approx 7.8$ Å, $a \approx 3.9$ Å) at 1.5 K, consistent with magnetic scattering at the X-point (0 ½ 0). We surmise that cation disorder across the A site disrupts the wider degrees of freedom in the system such that the desired irreps cannot be distinguished from the average structure alone. We posit that post-synthetic modifications to promote A site ordering could allow for the desired irreps to be identified, providing proof of concept that group theoretical approaches may be exploited to design new multiferroic materials.

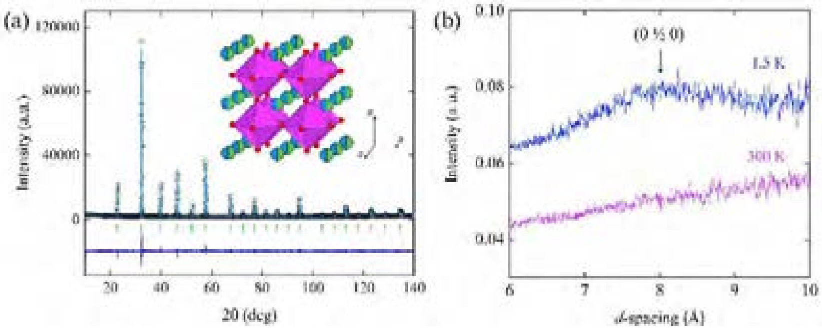


Fig. 1. (a) Rietveld fit of the $Pm\bar{3}m$ structural model against laboratory XRD data. **(b)** Comparison of the PND data collected at 1.5 K and 300 K. The arrow highlights the X-point (0 ½ 0) where magnetic diffuse scattering emerges.

References

[1] S. Jin et al., *Science*, 1994, **264**, 413-415. [2] T. Kimura et al., *Nature*, 2003, **426**, 55-58. [3] M. S. Senn and N. C. Bristowe, *Acta Cryst.*, 2018, A**74**, 308-321.

Discovery of the Novel Sustainable n-Type Thermoelectrics Zn2NX (X = Cl, Br, I) by Anion Mutation of ZnO

Kieran B. Spooner,[1,2] and David O. Scanlon[1-3]

[1] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom.

[2] Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, United Kingdom.

[3] Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom.

Thermoelectrics transform heat into electricity and vice versa, making them potentially valuable tools for the generation and recycling of clean, renewable energy. While progress has been made increasing their efficiency, measured by the dimensionless figure of merit, ZT, the best systems often contain rare or toxic elements, such as PbTe and Bi_2Te_3, which reduces their sustainable credentials. Furthermore, ZTs of *n*-type thermoelectrics have lagged behind those of their *p*-type counterparts, but both *n*- and *p*-type thermoelectrics are needed for a working device. Conductive oxides have shown promise as potential thermoelectrics[1] due to their strong electrical conductivity and high temperature stability, particularly ZnO, which has reached a ZT of 0.65 at 1000 K.[2] As they are often hindered by their high thermal conductivity, nanostructuring has been extensively tested for overcoming this problem,[3] but this limits the electrical conductivity as well as the thermal conductivity, reducing the potential ZT gains.

Here we use hybrid density functional theory (DFT) to screen the anion mutated ZnO derivatives Zn_2NX (X = Br, I)[4] for thermoelectric properties. We analyse their thermal and electronic transport beyond the constant relaxation time approximation (CRT) using Phono3py[5] and AMSET[6] respectively. We show that anion mutation is a highly effective means to increase the scattering of phonons, and so reduce the lattice thermal conductivity, and also analyse the effect on several electronic scattering mechanisms. We find high electrical conductivity is inherited from their parent, ZnO, while the lattice thermal conductivity is greatly reduced, leading to greatly enhanced ZT. We then use these insights to assess the potential of the anion mutation method.

References

[1] Spooner, K. B. *et al.*, Chem. Mater. **2021**, *33*, 7441.

[2] Ohtaki, M. *et al.*, J. Electron. Mater. **2009**, *38*, 1234.

[3] Spooner, K. B. *et al.*, J. Mater. Chem A **2020**, *8*, 11948.

[4] Liu, X. *et al.*, J. Solid State Chem. **2013**, *203*, 31.

[5] Togo, A., Tanaka, I., Phys. Rev. B **2015**, *91*, 094306.

[6] Ganose, A. M. *et al.*, Nat. Commun. **2021**, *12*, 2222.

Computational design of high-entropy disordered rock salt cathode materials

Alexander G. Squires,[1] David O. Scanlon[1]

[1] University College London & the Faraday Institution

Disordered rock salt oxyfluoride cathode materials are perceived as excellent candidates for application as future lithium-ion cathode materials enabling chemistries beyond commercial layered Ni-Mn-Co technologies [1]. Disordered rock salt cathodes can possess long-range "0-TM" percolation networks, which allow for fast and facile lithium diffusion, ensuring a good rate capability and high capacity [2]. Any short-range order (SRO) observed in these materials is typically associated with a reduced connectivity of these 0-TM networks [3]. Suppressing SRO in disordered rock salt cathode materials is therefore crucial to maximising their performance. Alloying many transition metals together across the cation sublattice, creating so-called high-entropy rock salts, has been proposed as a method for minimising SRO [4, 5]. This approach is expected to improve Li transport through the bulk by supressing the formation of a single dominant SRO type by increasing competition between a larger number of transition metal species [6]. While the high-entropy cathode concept has been shown to have initial promise, typically studies on these materials have not gone far beyond "proof of concept" stages; a deeper understanding of the relationship between configurational entropy, compositional chemistry and SRO suppression is lacking. This poses an exciting materials design challenge which requires an understanding of the independent effects of the number and concentration of different transition metals on the cation sublattice and the fluorine content on the anion sublattice and how these variables combine to determine the observed SRO in as-synthesised cathode materials. An understanding of these different concepts will aid in identifying low-cost, high-entropy rock salt compositions which possess excellent electrochemical performance. In this work we use cluster-expansion parameterised Monte Carlo simulations to examine the connectivity of the Li percolation network when varying the composition of high-component DRX Li cathode materials. We reveal the relative importance of the specific composition of the system as compared to a general increase in the configurational entropy and derive design rules for performant many-component disordered rock salt oxyfluoride cathode materials.

References

1. Clément, R. J. et al. 2020. "Cation-Disordered Rocksalt Transition Metal Oxides and Oxyfluorides for High Energy Lithium-Ion Cathodes." *Energy & Environmental Science* 13 (2): 345–73.
2. Lee, Jinhyuk et al. 2014. "Unlocking the Potential of Cation-Disordered Oxides for Rechargeable Lithium Batteries." *Science* 343 (6170): 519–22.
3. Ji, Huiwen, et al. 2019. "Hidden Structural and Chemical Order Controls Lithium Transport in Cation-Disordered Oxides for Rechargeable Batteries." *Nature Communications* 10 (1): 592.
4. Wang, Qingsong, et al. 2019. "Multi-Anionic and -Cationic Compounds: New High Entropy Materials for Advanced Li-Ion Batteries." *Energy & Environmental Science* 12 (8): 2433–42.
5. Sarkar, Abhishek, et al. 2018. "High Entropy Oxides for Reversible Energy Storage." *Nature Communications* 9 (1): 3400.
6. Lun, Zhengyan, et al. 2021. "Cation-Disordered Rocksalt-Type High-Entropy Cathodes for Li-Ion batteries." *Nature Materials* 20 (2): 214–21.

Bulk and Local Structural Evolution During Electrochemical Cycling in $NaNiO_2$

James M. A. Steele,[1] Joshua D. Bocarsly,[1] Siân E. Dutton[2] and Clare P. Grey.[1]

[1] Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom,

[2] Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, United Kingdom.

Jahn-Teller distortions, layer glides, and charge ordering during cathode cycling often lead to battery degradation over time. Sodium Nickel Oxide ($NaNiO_2$) serves as a model compound for nickel-rich materials, featuring a Ni^{3+} Jahn-Teller (JT) active ground state, and a plethora of phase transitions during cycling as nickel is oxidised to Ni^{4+}. However, so far, the structural evolution of this material and the behaviour of the JT distortion have not been fully understood. Nominally, a series of distorted octahedral (O'ˣ3) and prismatic (P'ˣ3) phases form throughout charge/discharge.[1–3] Here, we utilised *in/ex situ* synchrotron X-ray Diffraction (XRD) and solid-state nuclear magnetic resonance (ssNMR) to determine the long- and short-range structure of $NaNiO_2$ as it charges and discharges. Complementary bulk and local characterisation allowed investigation of Na^+ vacancy ordering, JT distortion, and structural irreversibilities which occur during charge and discharge cycles. A previously unreported phase (O''''3) was identified in ssNMR and XRD. ssNMR confirmed that complete reversibility back to the fully sodiated parent O'3 phase does not occur upon discharge. Understanding of the physical processes which occur during cycling of $NaNiO_2$, and the resultant effect on cathode electrochemistry, will inform the design of novel high-performance, nickel-rich Na^+ ion cathodes with suitable capacity and lifetime for practical applications in large-scale grid storage.

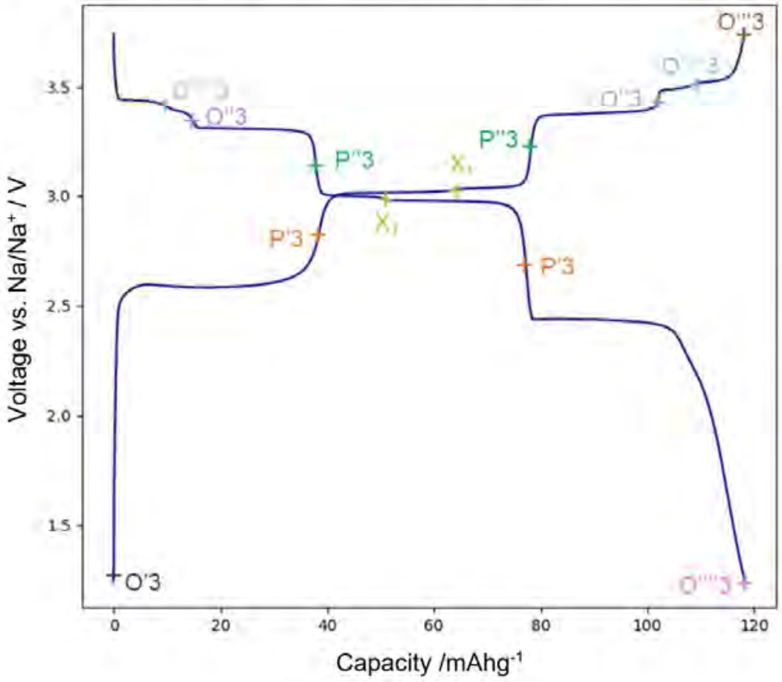


Figure 1: The electrochemical voltage profile for a $NaNiO_2$ half cell (with Na metal anode) between 1.25 – 3.75 V, showing the evolution of phases as the battery is cycled.

References

[1] P. Vassilaras, X. Ma, X. Li and G. Ceder, *J. Electrochem. Soc.*, 2012, **160**, A207.
[2] M. H. Han, E. Gonzalo, M. Casas-Cabanas and T. Rojo, *J. Power Sources*, 2014, **258**, 266–271.
[3] L. Wang, J. Wang, X. Zhang, Y. Ren, P. Zuo, G. Yin and J. Wang, *Nano Energy*, 2017, **34**, 215–223.

Chemical displacements drive the physical properties in a new Bi-based relaxor-ferroelectric system

T. Wesley Surta,[1,2] Lynette Keeney,[3] Alicia M. Manjon-Sanz,[4,5] Catriona Crawford,[1] Alexandra Morscher,[1] Luke M. Daniels,[1] John B. Claridge,[1,2] Andrew J. Bell,[6] Jonathan Alaria,[7,2] Matthew J. Rosseinsky.[1,2]

[1] Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, UK
[2] Leverhulme Centre for Functional Materials Design, The Materials Innovation Factory, University of Liverpool, 51 Oxford Street, Liverpool L7 3NY, UK
[3] Tyndall National Institute, Lee Maltings Complex Dyke Parade, Cork, Cork, T12 R5CP, Ireland
[4] CELLS–ALBA synchrotron, Cerdanyola del Vallés, Barcelona E-08290, Spain
[5] Neutron Scattering Division, Oak Ridge National Lab, Oak Ridge, Tennessee 37831, USA
[6] Department of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK
[7] Department of Physics, University of Liverpool, Oxford Street, Liverpool L69 7ZE, UK

Piezoelectric materials are vital components of the modern technological landscape, enabling devices ranging from actuators for diesel fuel injectors to sensors for 5G phones. The industrial standard material is a perovskite oxide solid solution, $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), but concerns over the health and environmental impacts of Pb-based electronics has motivated the search for an alternative. Design by analogy to PZT has yet to yield a viable candidate. However, there is a superior Pb-based piezoelectric from which to draw analogy, the solid solution between $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $PbTiO_3$ (PMN-PT). As a ceramic PMN-PT has a piezoelectric figure of merit (d_{33} = 720 pm/V), larger than PZT (d_{33} = 200-640 pm/V), and an anomalous enhancement when in single crystal form, reaching d_{33} values of 4100 pm/V in doped samples.[1–3]

I will present our work on the first Pb-free PMN-PT analogue: $(1-x)(K_{1/2}Bi_{1/2})(Mg_{1/3}Nb_{2/3})O_3-x(K_{1/2}Bi_{1/2})TiO_3$ (KBMN-KBT). One key difference between PZT and PMN-PT is the relaxor properties of the PMN endmember. Relaxors have a centrosymmetric average structure, but local displacements which confer non-centrosymmetric properties. Our KBMN endmember is determined to be a relaxor (Figure 1a) with many similarities with PMN that are driven by disordered Bi^{3+} displacements.[4] We further identify the structural origin driving the quantitative differences in properties between KBMN and PMN.

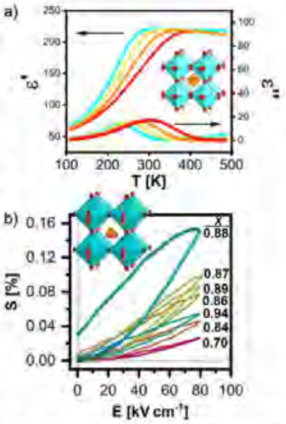


Figure 1: a) Dielectric permittivity as function of temperature of KBMN showing relaxations. b) Lattice strain as a function of electric field showing increased performance at x = 0.88. The refined crystal structures are inset.

The other difference between PZT and PMN-PT is the symmetries which generate an enhanced d_{33}. Our compositional optimization of KBMN-KBT reveals the same progression of symmetries as those in PMN-PT. Furthermore, piezoelectric strain measurements (Figure 1b) reveal the properties are enhanced at x = 0.88, to a value of 192 pm/V, which mirrors the structure-properties relationships in PMN-PT. Furthermore, we determine that the local Bi^{3+} displacements persist through multiple changes in symmetry and continue to drive the properties. A suite of measurements generates a multiple length-scale perspective, isolating the underlying mechanism driving this physical response. This work serves as a proof of concept that a PMN-PT based design strategy is a viable method for designing Pb-free piezoelectrics and generates insights into how the bonding preference of Bi^{3+} can be used to manipulate the structure and properties of materials.

References

[1] Kelly, M. Leonard, C. Tantigate, A. Safari, *J. Am. Ceram. Soc.* 1997, ***80***, 957.
[2] B. Jaffe, W. R. Cook, H. L. Jaffe, *Piezoelectric Ceramics*, Academic Press, New York, 1971.
[3] F. Li, et al, *Science*. 2019, ***364***, 264.
[4] T. W. Surta, et al, *J. Am. Chem. Soc.* 2021, **143**, 1386.

A Computational Study of the Intrinsic Defect Chemistry of Promising Sodium-Ion Cathode Material Na_2FePO_4F

Daniel Sykes,[1,2] Yong-Seok Choi[1,2] and David O. Scanlon.[1,2,3]

[1] University College London, London, United Kingdom,

[2] Faraday Institution, Didcot, Oxfordshire, United Kingdom,

[3] Diamond Light Source, Didcot, Oxfordshire, United Kingdom.

Long-term viability of Li-ion battery energy storage may be limited by global lithium reserves. Recently, sodium-ion batteries (NIBs) have garnered a great deal of attention, partially because of sodium's natural abundance, its more even distribution across the earth and it costs less than lithium. NIBs are especially attractive for large-scale energy storage systems where cost and life cycle are essential. To this end, Na_2FePO_4F has been a material of interest as a viable cathode material for sodium-ion storage due to the high discharge voltage and favourable theoretical capacity.[1] Recent work has shown the potential for doping in Na_2FePO_4F cathodes to increase average e voltage, reduce band gap and Na-ion diffusion barrier.[2]

In this work we will present work completed on computationally investigating Na_2FePO_4F using Density Functional Theory (DFT) with the periodic code, VASP (Vienna Ab Initio Simulation Package), and the hybrid HSE06 (Heyd-Scuseria-Ernzerhof) functional.[3] Here we elucidated the bulk geometric structure of the material through relaxation as well as the most stable magnetic configuration. The electronic structure of the material has also been examined with a Density of States (DOS) and band structure being obtained. In order to examine the defect landscape of the material effectively, the different stable phases of Na_2FePO_4F have been investigated. Calculating the phase stability of Na_2FePO_4F builds a foundation for a detailed understanding of its defect chemistry at given chemical potentials.

The intrinsic vacancy defects for the Na_2FePO_4F system have been calculated with Hybrid DFT and the formation energies of these vacancies have been plotted at the systems relevant stability limits across its band gap. There has also been significant work completed on examining the manner of how localised charges form in these vacancies and how this affects their energies.

References

1. B. L. Ellis, W. R. M. Makahnouk, Y. Makimura, K. Toghill, L. F. Nazar, *Nature Mater*, **2007**, 6, 749-753
2. D. Jin, H. Qui, F Du, Y. Wei, X Meng, *Solid State Sciences*, **2019**, 93, 63-69
3. A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, G. E. Scuseria, J. *Chem. Phys.*, **2006**, 6, 224106

High Voltage Cathode Materials for Next-Generation Magnesium Ion Batteries

Camilla Tacconis,[1] Dr Sunita Dey,[2] Prof Clare Grey[2] and Prof Siân Dutton.[1]

[1] Cavendish Laboratory, J Thomson Ave, Cambridge CB3 0HE, UK,
[2] Yusuf Hamied Department of Chemistry,12 Union Rd, Cambridge CB2 1EZ, UK.

Magnesium presents a promising replacement to Lithium in Next Generation Rechargeable batteries. Cheaper, more abundant and safer than Li, Mg's divalence further promises the production of cells with higher gravimetric capacities. However, the technology is at an early stage of research with many issues still unresolved; including the lack of cathode candidates with sufficiently high operating voltages and favourable ionic kinetics.[1]

A previous Bond Valence Sum (BVS) study identified the family of pyroborates $Mg_xFe_{1-x}B_2O_5$ as promising high voltage cathodes with percolating diffusion channels insensitive to ionic disorder and accessible at room temperature.[2] We have synthesised $MgFeB_2O_5$ and characterised the crystal structure using refinement of Synchrotron PXRD data. Galvanostatic cycling of the cathode vs Li metal anode demonstrated capacities close to the maximum expected theoretical value of 294.9 mAh g^{-1}. A Variety of techniques such as XANES, XPS, Curie-Weiss fitting and SEM have been adopted to evaluate whether such promising capacities can be attributed to Mg^{2+} mobility within the cathode material.

This work presents a thorough investigation of the electrochemical processes and structural properties that could accommodate for Mg ion removal from the host network of the $MgFeB_2O_5$ cathode. Merging solid state and electro- chemistry, we highlight the often overlooked complexity in probing Magnesium ionic motion, discussing the strengths and weaknesses of the techniques adopted so far in this study.

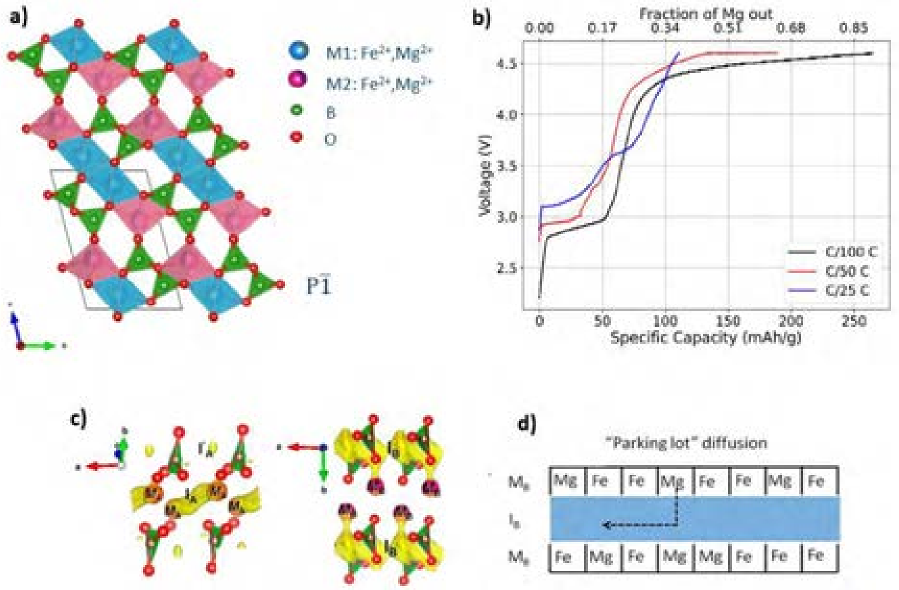


Figure 1. (a) Refined crystal structure for $MgFeB_2O_5$ obtained from Rietveld refinement of Synchrotron PXRD, (b) galvanostatic cycling of coin cells at 55ºC, (c) BVS map[2] for the crystal structure highlighting the percolating diffusion channels and (d) illustrates robustness of the channels to disorder on the metal sites M1 and M2 through the parking lot analogy.[2]

References

[1] Saha et al., Progress in Materials Science, 66, (2014), 1-86
[2] Bo S. et al., Chemistry of Materials, 27, (2015), 4630-4639

EFFECT OF FLUORINE ON THE INTERFACIAL RESISTANCE IN ARGYRODITE BASED SOLID STATE BATTERIES

Chris I. Thomas ,[1,2] Sebastian J. Altus,[1,2] Enrique Sánchez Pérez, [1,2] Edmund J. Cussen[1,2], and Serena A. Cussen.[1,2]

[1] Department of Materials Science and Engineering, University of Sheffield.

[2] The Faraday Institution, Quad One, Harwell Science and Innovation Campus.

.

Battery devices have infiltrated every aspect of our lives from hand held devices to vehicles. However conventional Li-ion technology makes use of a toxic flammable liquid electrolyte which raises a variety of safety concerns that could hinder the large scale adoption within several industries. Further limitations arise when considering the specific energy of a current Li-ion battery (246 Wh kg^{-1}), which is significantly off the DoE target of 500 Wh kg^{-1} by 2030.

Solid State batteries could overcome these challenges by using metallic lithium anodes rather than the intercalated graphite anodes currently used for Li-ion batteries. The theoretical capacity of a metallic lithium solid state battery (3860 mAh g^{-1}), the low reduction potential (-3.040 V) and replacing the flammable liquid organic electrolyte all hold the potential for significant improvements in the safety, energy, and power densities so highly desired by industry.

Extensive research into the solid electrolyte has yielded high Li+ conductivity (>10^{-4} S cm^{-1}) oxides, polymers and sulphides close to liquid electrolyte performance.[1,2] Of particular interest are the argyrodite-structured sulphides with the general formula Li_6PS_5X (X = Cl, Br, I). A significant challenge however is sulphide argyrodites exhibit stability issues with respect to metallic lithium. Recent investigations have however shown that the addition of fluoride may address these concerns by stabilising the anode-electrolyte interface.[3] In this work we investigate the solid-state electrolyte formed from the argyrodite target composition $Li_6PS_5F_{0.5}Br_{0.5}$. Exhibiting a Li-ion conductivity of 5 x10^{-5} S cm^{-1} (30°C) under no external pressure we observe that the inclusion of fluoride allows for the reduction and stabilisation of the lithium metal argyrodite interface thereby effecting achievable current densities.

References

1 M. Pasta, D. Armstrong, C.I. Thomas et al. *J. Phys. Energy*. 2020, **2** ,32008.

2 T. A. Schmaltz, T. Wicke, L. Weymann et al., *Solid-State Battery Roadmap 2035+*, 2022 1–112.

3 W. Arnold, V. Shreyas, Y. Li et al. *ACS Appl. Mater. Interfaces*. 2022, **14 ,**11483–11492.

Ab initio models of orientational disorder and phase transitions in hybrid piezoelectric materials

Kasper Tolborg[1] and Aron Walsh[1]

[1] Department of Materials, Imperial College London, Exhibition Road, SW7 2AZ,
United Kingdom

Piezoelectric materials interconverting electrical and mechanical energy find applications in diverse areas as sensors, actuators, and high precision motors. Current state-of-the-art piezoelectric materials are made from lead-based ceramics, which pose significant environmental issues and precludes design of biocompatible devices. Recent progress in molecular and hybrid organic-inorganic piezoelectric materials have led to discovery of new materials with properties rivalling the lead-based ceramics, and with the additional prospects of being solution processable, flexible, and potentially biocompatible.[1,2] However, conventional computational methods fail to predict their large piezoelectric response,[3] and pertinent phase transitions to disordered, centrosymmetric phases appear near or above room temperature, which may hamper their practical applications. Thus, proper computational modelling of this materials class must include nanoscale effects for response properties, and entropic effects to phase stability.[4]

Here, we present the development of an ab initio model for the ordering of dipolar molecules in the high-performance hybrid piezoelectric material, $TMCMCdCl_3$ (TMCM = trimethylchloromethyl ammonia). Based on a model Hamiltonian fitted to density functional theory (DFT) data and Monte Carlo simulations, we predict and rationalise its order-disorder ferroelectric-to-paraelectric phase transition. We show that a model Hamiltonian based on internal energies calculated from DFT fails to quantitatively reproduce phase transition temperatures, whereas inclusion of vibrational free energy effects improves the agreement with experiment significantly. This highlights the importance of vibrational entropy in describing phase stability for a materials class seemingly driven by configurational entropy.[5]

Besides prediction of phase stability, our model Hamiltonian also provide insights into the strong piezoelectric response, which can be attributed to easy formation of orientational defects and intergrowths.

References

[1] Y.-M. You, W.-Q. Liao, D. Zhao et al., *Science*, 2017, **357**, 306-309
[2] W.-Q. Liao, D. Zhao, Y.-Y. Tang et al., *Science*, 2019, **363**, 1206–1210.
[3] P. S. Ghosh, S. Lisenkov and I. Ponomareva, *Phys. Rev. Lett.*, 2020, **125**, 207601
[4] K. Tolborg, J. Klarbring, A. Ganose and A. Walsh, *RSC Digital Discovery*, 2022, **1**, 586-595
[5] K. Li, Z.-G. Li, J. Xi et al., *J. Am. Chem. Soc.*, 2022, **144**, 816-823

Interplay of Jahn-Teller distortions, orbital order and structural degrees of freedom in $LaMn_{1-x}Ga_xO_3$

Benjamin R. M. Tragheim[1] and Mark S. Senn[1]

[1] Department of Chemistry, University of Warwick, Coventry, CV4 7AL.

Understanding the emergence of colossal magnetoresistance (CMR) in the doped manganites $La_{1-x}Ca_xMnO_3$ (LCMO) is an active, ongoing area of research in solid-state chemistry due to its potential technological applications in novel data storage devices. Maximal CMR, occurring at x = 3/8, is believed to be caused by phase segregation between metallic orbital disordered and insulating orbital ordered states.[1] Orbital order here closely resembles that of *C*-type orbital order in $LaMnO_3$, intimately tied to cooperative Jahn-Teller (JT) distortions (Figure 1). Understanding these orbital phenomena are therefore key in the design and optimisation of new functional materials. However, due to many control factors occurring in LCMO about this optimal doping regime including phase segregation, mixed Mn oxidation states, electronic band-narrowing and octahedral tilting, it is difficult to ascertain an accurate in-depth microstructural understanding of how orbital ordering phenomena arise in CMR materials. Hence, the use of prototypic systems helps to discern these phenomena by disentangling the competing complexities. From this, we have previously shown using quadruple perovskites of the form AMn_7O_{12} ($A = Na_{1-x}Ca_x$, $La_{1-x}Ca_x$) that at x = 3/8, coincident with the optimal doping level in CMR manganites, we discover a novel striping of orbital order and charge disorder in a 1:3 ratio along the [1 0 -1] plane not observed before.[2] This discovery gives new insight into the missing intermediate state between insulating and metallic phases in CMR materials.

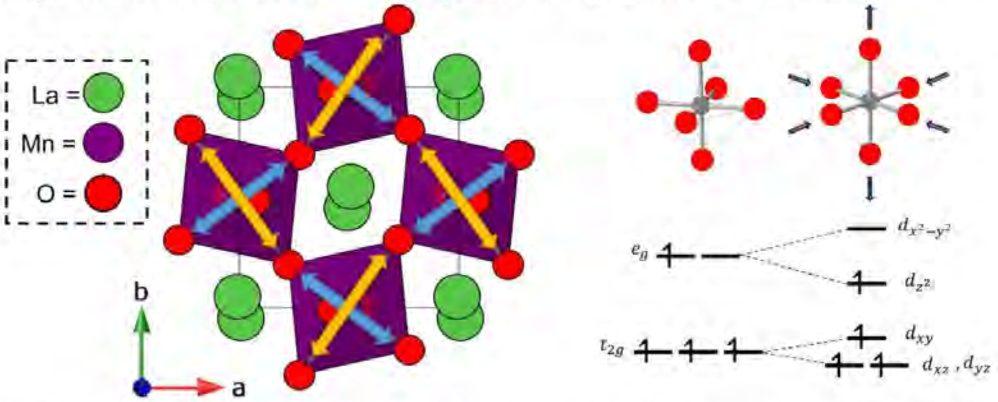


Figure 1: (left) C-type orbital order in low temperature $LaMnO_3$ and orbital ordered LCMO phases – Yellow and blue arrows represent directions of long and short Mn-O bonds, respectively. (right) Schematic of the Jahn-Teller effect in isolated MnO_6 octahedra.

$LaMn_{1-x}Ga_xO_3$ proves to be an ideal system for observing orbital order-disorder phenomena in the manganites, avoiding many of the complications described for LCMO. Substitution of JT-active Mn^{3+} for JT-inactive Ga^{3+} demonstrates a compositionally-induced orbital order-disorder transition in the range $0.4 \leq x \leq 0.6$ at ambient conditions, with a change in unit cell metric from orthorhombic to 'pseudocubic' similar to that observed in LCMO and the high temperature $LaMnO_3$ orbital order transition. This regime is close to the substitution level x = 3/8 in which we have observed novel orbital order-charge disorder striping in AMn_7O_{12} quadruple perovskites and coincident with maximal CMR in LCMO (x = 3/8), meaning that there is a great precedent to study this transition in precise crystallographic detail. We therefore present synchrotron Bragg and total scattering data investigating both the average and local structure, respectively, of the solid-solution $LaMn_{1-x}Ga_xO_3$ to decouple the interplay between JT distortions, orbital order and structural degrees of freedom. Data analysis is tackled using the powerful tool symmetry-mode analysis which gives further crystallographic insight into subtle structural distortions occurring in these materials, and how different modes couple together to drive aforementioned phase transitions due to orbital phenomena.

References: [1] C. H. Chen, S. W. Cheong, S. Mori and M. Uehara, *Nature*, 1999, **399**, 560-563. **[2]** W.-T. Chen, C.-W. Wang, C.-C. Cheng, Y.-C. Chuang, A. Simonov, N. C. Bristowe and M. S. Senn, *Nat. Commun.*, 2021, **12**, 1–8.

Electron-lattice interaction in antimony chalcogenide semiconductors

Xinwei Wang [1], Alex M. Ganose [1], Seán R. Kavanagh [1,2], Aron Walsh [1]

[1] Department of Materials, Imperial College London, UK

[2] Thomas Young Centre and Department of Chemistry, University College London, UK

Abstract:

Antimony chalcogenides (Sb_2X_3; X = S, Se) have emerged as promising earth-abundant alternatives among thin-film photovoltaic compounds due to their significant electronic and optical advantages. Despite the rapidly increasing solar conversion efficiencies in Sb_2X_3 since their discovery, the record efficiencies (7.5% and 9.2% for Sb_2S_3 and Sb_2Se_3 solar cells, respectively[1,2]) are far from satisfactory and have stagnated for a few years. Among the factors limiting efficiencies, charge carrier dynamics play a vital role. However, whether the photoexcited carriers in Sb_2X_3 are intrinsically self-trapped or trapped at extrinsic defect sites is under debate[3,4], and the theoretical study of carrier transport in Sb_2X_3 remains unexplored.

In this work, building on our analysis of anisotropy in the Fermi surfaces[5], the electron-lattice interaction and carrier transport properties in Sb_2X_3 were investigated *ab initio*. Our results show that both Sb_2S_3 and Sb_2Se_3 have intermediate Fröhlich coupling constants (~2), large polaron radii (extend over more than one unit cell) and large mobilities (> 10 cm^2/Vs at room temperature for both electrons and holes), indicating that electron and hole polarons prefer to delocalise rather than localise. Electron and hole polarons were also modelled by systematic first-principles calculations, which further confirm that large polarons instead of small polarons (i.e. self-trapped carriers) are more likely to form intrinsically in Sb_2X_3.

References

[1] Choi Y C, Lee D U, Noh J H, et al. *Advanced Functional Materials*, 2014, **24(23)**: 3587-3592.

[2] Li Z, Liang X, Li G, et al. *Nature Communications*, 2019, **10(1)**: 1-9.

[3] Yang Z, Wang X, Chen Y, et al. *Nature Communications*, 2019, **10(1)**: 1-8.

[4] Grad L, von Rohr F O, Hengsberger M, et al. *Physical Review Materials*, 2021, **5(7)**: 075401.

[5] Wang X, Li Z, Kavanagh S R, et al. *Physical Chemistry Chemical Physics*, 2022, **24(12)**: 7195-7202.

LLZO outside of the glovebox – Carbonation of LLZO, its effect on electrical properties, and how to remove it

James Watt,[1] Professor Derek Sinclair[2] and Dr Brant Walkley[3]
[1,2] University of Sheffield, Functional Materials and devices,
[3] University of Sheffield, Sustainable materials at Sheffield Group.

Lithium Lanthanum Zirconate (LLZO) has been of great interest for years as a potential candidate for all solid-state lithium ion batteries due to its promising lithium conductivity in the region of x10^{-4} S cm^{-1} [1]. Despite its promising lithium conductivity, a multitude of difficulties have been reported including but not limited to its sensitivity to moisture and ambient atmosphere. It has been reported that when exposed to the ambient atmosphere LLZO undergoes a multistep process to form a surface layer of Li_2CO_3 [2]. This layer is easily observable using raman spectroscopy, with Li_2CO_3 producing a characteristic peak at 1100 cm^{-1} [3]**.** Because of this historically LLZO is handled in glove-boxes to prevent contact with air, but that doesn't lend itself to mass manufacture. Utilising the thermal decomposition of Li_2CO_3 this work shows how significant Li_2CO can be almost entirely removed with a thermal treatment. This thermal treatment on powder removes surface Li_2CO_3 which dramatically improves densification behaviour of the material. This work saw an increase in density from ~70% to ~90% of theoretical upon thermal treatment of the powder. The pellet was left to age in air for a week which caused a drop in electrical conductivity from 1.7x10^{-4} S cm^{-1} to 1.73x10^{-5} S cm^{-1}. Raman spectroscopy showed that Li_2CO_3 had formed over the course of this week inhibiting the conductivity of Al-LLZO. Utilising a 900C thermal heat treatment under flowing nitrogen the formed Li_2CO_3 could be removed in its entirety returning the electrical properties back to a more desirable conductivity of 3.06x10^{-4} S cm^{-1}.

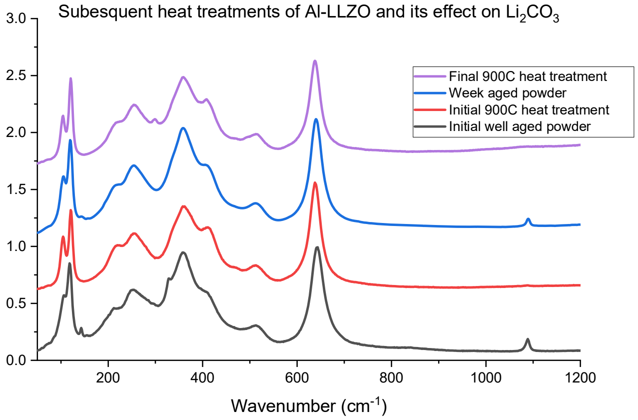


Figure 6. Displays the results of performing 900°C heat treatments as a method of removing Li_2CO_3 from LLZO that has been in contact with air. The graph shows the initial powder containing significant levels of LI_2CO_3 which can subsequently removed using further thermal processing. Once in pellet form the smaple is shown to age and then be 'refreshed' once again.

[1] C. Shao, H. Liu, Z. Yu, Z. Zheng, N. Sun, and C. Diao, "Structure and ionic conductivity of cubic Li7La3Zr2O12 solid electrolyte prepared by chemical co-precipitation method," *Solid State Ionics*, vol. 287, pp. 13–16, Apr. 2016.

[2] Melanie Rosen *et al.*, "Controlling the lithium proton exchange of LLZO to enable reproducible processing and performance optimization," *J. Mater. Chem. A*, vol. 9, no. 8, pp. 4831–4840, Mar. 2021.

[3] A. Sharafi *et al.*, "Impact of air exposure and surface chemistry on Li-Li7La3Zr2O12 interfacial resistance," *J. Mater. Chem. A*, vol. 5, no. 26, pp. 13475–13487, Jul. 2017.

Computational Prediction and Experimental Realisation of Earth-Abundant Transparent Conducting Oxide Ga-Doped $ZnSb_2O_6$

Joe Willis[1,2] and David O. Scanlon

[1] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom,

[2] Thomas Young Centre, University College London, Gower Street, London, WC1E 6BT, United Kingdom.

Transparent conducting oxides have become ubiquitous in modern opto-electronics. However, the number of oxides that are transparent to visible light and have the metallic-like conductivity necessary for applications is limited to a handful of systems that have been known for the past 40 years.

Here, we use hybrid density functional theory and a full defect chemistry analysis to demonstrate that $ZnSb_2O_6$ is an ideal transparent conducting oxide comprised of earth-abundant elements, and we identify gallium as the optimal dopant to yield high conductivity and transparency.[1] We simulate charge transport properties, such as electron mobility and scattering rates, using the AMSET code,[2] and calculate the electron affinity of $ZnSb_2O_6$ from first principles.

To validate our computational predictions, we have synthesised both powder samples and single crystals of Ga-doped $ZnSb_2O_6$ which conclusively show behaviour consistent with a degenerate transparent conducting oxide. We calculate a transparent conductor figure of merit on par with industry standard Sn-doped In_2O_3.This powerful theory-experiment collaboration emphasises the rôle of defects and defect control in semiconductors, and demonstrates the possibility of a family of Sb(V)-containing oxides for transparent conducting oxide and power electronics applications.

References

[1] Jackson, A. J. et al, *ACS Energy Letters*, 2022, **7**, 3806

[2] Ganose, A. M. et al, *Nat. Commun.*, 2021, **12**, 2222

Spark plasma sintering process for preparation of thermoelectric materials

Jianwei Xu,[1,2] Xian Yi Tan[1]

[1] Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634

[2] Institute of Sustainability for Chemicals, Energy and Environment, Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Jurong Island, Singapore 627833

Email: jw-xu@imre.a-star.edu.sg; Xu_Jianwei@isce2.a-star.edu.sg

Sintering is the process of forming a solid mass of material using heat and pressure without melting it completely to the liquid state. Particles or atoms in materials diffuse across particle boundaries and fuse together to form one piece during this process. Sintering is an integral step in the preparation of polycrystalline bulk inorganic materials from their loose powdered form, and it has been widely used to prepare inorganic-based thermoelectric materials. In this talk, the working principles of the spark plasma sintering method will be briefed, while the rationale behind its great popularity in the thermoelectric material research field will be discussed. Various techniques, such as modifications to the sintering conditions, introduction of liquid-phase additives, and texture engineering, will be reviewed. Their effects on the grain orientation, microstructural defects, and thermoelectric performance of the resulting pellet materials will also be discussed. A cheaper and less energy-intensive alternative to the spark plasma sintering method for densifying inorganic material powders into pellets will be mentioned.

References

[1] X Wang, Y Zheng, A Suwardi, J Wu, SL Teo, Q Zhu, G Wu, J Xu, *Materials Chemistry Frontiers*, 2022, **6**, 2468-2477.

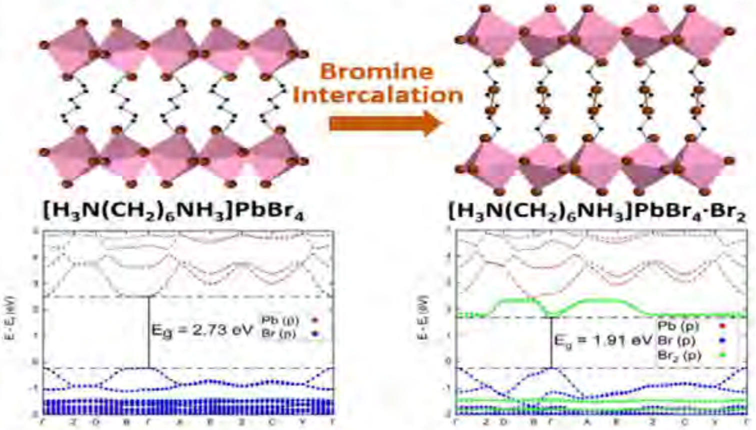
[2] X Wang, A Suwardi, Y Zheng, H Zhou, SW Chien, J Xu, *ACS Applied Nano Materials* 2020, **3**, 10156-10165.

Manipulation of the optoelectronic properties of layered hybrid perovskites by molecular intercalation

Lin-Jie Yang[1], Wenye Xuan[2,3], David Webster4, Lethy Krishnan Jagadamma[4], Teng Li[1], David N. Miller[1], David B. Cordes[1], Alexandra M. Z. Slawin[1], Graham A. Turnbull[4], Ifor D. W. Samuel[4] , Hsin-Yi Tiffany Chen[3], Philip Lightfoot[1], Matthew S. Dyer[2], Julia L. Payne[1*]
[1]School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST
[2]School of Chemistry, University of Liverpool, Crown St, Liverpool, L69 7ZD
[3]Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan.
[4]Organic Semiconductor Centre, School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9SS

Layered hybrid perovskites have received considerable attention due to the high tunability of their crystal structures, which in turn influences their physical properties. To the best of our knowledge more than 840 different hybrid layered perovskites have been reported[1] and many of these have been tested in solar cells[2], X-ray detectors[3] and other optoelectronic devices. However, layered hybrid perovskites with single inorganic sheets (denoted as $n = 1$) are hardly considered as light absorbers in solar cells, despite good stability in air or humid atmospheres, due to their large bandgap (E_g) and high exciton binding energy (E_b). To develop layered hybrid perovskite solar cells, most scientists chose hybrid perovskites with multiple inorganic sheets and the highest efficiency achieved for these is currently 21.07%[4].

Here, an alternative method is used to decrease the E_g of traditional $n = 1$ perovskites: using halogen molecule intercalation. For example, a bromine molecule could be inserted between the inorganic layers of the hybrid perovskite $[H_3N(CH_2)_6NH_3]PbBr_4$ and was stabilised by the formation of halogen bonds between Br_2 and the $PbBr_6$ containing inorganic layer. Crystallographic and computational studies were used to show that a new conduction band was provided by the guest bromine molecules during the intercalation. Also, a significant decrease in effective mass was observed. Therefore, compared with $[H_3N(CH_2)_6NH_3]PbBr_4$, the resulting crystalline material, $[H_3N(CH_2)_6NH_3]PbBr_4{\cdot}Br_2$, has greatly lower bandgap and resistivity and a higher mobility/ charge carrier concentration. Additionally, $[H_3N(CH_2)_6NH_3]PbBr_4{\cdot}Br_2$ has considerable stability in humid atmospheres, which suggests that intercalation could be a potential method to design new photovoltaic materials[5].



1 E. I. Marchenko, S. A. Fateev, A. A. Petrov, V. V. Korolev, A. Mitrofanov, A. V. Petrov, E. A. Goodilin and A. B. Tarasov, *Chem. Mater.*, 2020, **32**, 7383–7388.
2 M. He, J. Liang, Z. Zhang, Y. Qiu, Z. Deng, H. Xu, J. Wang, Y. Yang, Z. Chen and C. C. Chen, *J. Mater. Chem. A*, 2020, **8**, 25831–25841.
3 J. Peng, C. Q. Xia, Y. Xu, R. Li, L. Cui, J. K. Clegg, L. M. Herz, M. B. Johnston and Q. Lin, *Nat. Commun.*, 2021, **12**, 1–10.
4 M. Shao, T. Bie, L. Yang, Y. Gao, X. Jin, F. He, N. Zheng, Y. Yu and X. Zhang, *Adv. Mater.*, 2021, **34**, 1.
5 L-J. Yang, W. Xuan, D. Webster, L. K. Jagadamma, T. Li, D. N. Miller, D. B. Cordes, A. M. Z. Slawin, G. A. Turnbull, I. D. W. Samuel, H-Y. T. Chen, P. Lightfoot, M. S. Dyer and J. L. Payne, *Chem. Mater.*, submitted.

The Thermal Properties of Hybrid Organic-Inorganic Perovskites (HOIPs)

Chumei Ye,[1] Lauren N. McHugh,[1] Siân E. Dutton,[2] and Thomas D. Bennett.[1]

[1] Department of Materials Science and Metallurgy, University of Cambridge, UK,

[2] Department of Physics, University of Cambridge, UK.

The past decade has witnessed an explosion of interest in the research field of HOIPs, whose general chemical formula is ABX_3, in which A is a monovalent organic cation, B is a metal ion (typically Pb), and X is an anion six-coordinated with B[1]. Recently, research has tended to focus on nontoxic lead-free perovskites for environmental viability, where the traditional halide X-site ligands are replaced by functional organic bridging linkers such as dicyanamide[2], formate[3] and thiocyanate[4]. These materials are thus more akin to metal-organic frameworks (MOFs) than their parent perovskite compounds. Amongst them, it has been found that dicyanamide-based HOIPs can melt and form melt-quenched glasses that show intriguing thermal and electrical conductivities[2]. Additionally, a novel class of HOIPs with two-dimensional (2D) A_2BX_4 structures are known for their enhanced stability. Until now, most research in HOIPs has concentrated on improving their optoelectronic properties. Investigation into their thermal properties is, however, also of high significance, offering opportunities to develop structure-property relationships and improve applicability.

Formate and thiocyanate were individually incorporated into three-dimensional (3D) HOIPs as an X-site anion, an 2D HOIPs was constructed using (S)-(-)-1-(1-naphthyl)ethylamine as an A-site cation, and their components and phase transitions in response to temperature are studied herein (Figure 1). More comprehensively, it is evident that formate-based HOIPs, i.e. $[Am]Mn(HCOO)_3$ (Am = imidazolium and formamidinium) exhibit a two-step mass loss with increasing temperature, and the resulting phase at each step is calculated. For the thiocyanate-based HOIPs $[Am]x\{Ni[Bi(SCN)_6]\}$ (Am = potassium, ammonium and guanidinium), the effect of different A-site cations on thermal properties is studied and impurities are identified through DSC and variable-temperature XRD characterization. Moreover, the melting and glass-forming process of 2D dimensional S-NPB perovskites are discussed. This research may contribute to understanding the thermal and glass-forming behaviours of HOIPs with various A-site cations and X-site anions.

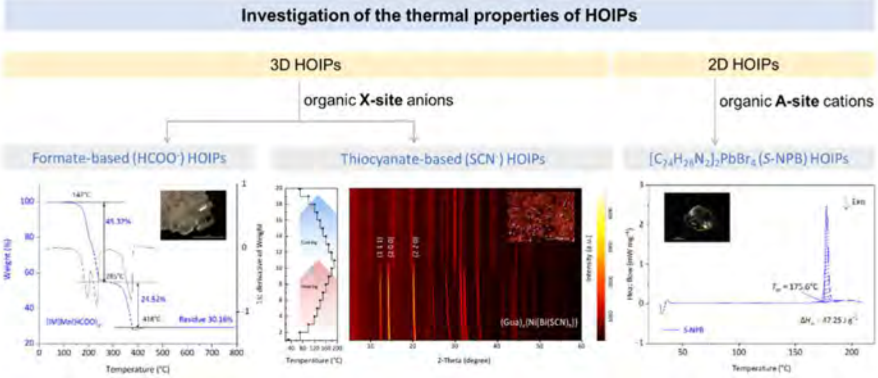


Figure 1 TOC for research.

References

[1] W. Li, Z. Wang, F. Deschler, S. Gao, R. H. Friend, A. K. Cheetham. *Nat. Rev. Mater.*, 2017, **2**, 99.

[2] B. K. Shaw, A. R. Hughes, M. Ducamp, et al. *Nat Chem.*, 2021, **13**, 778.

[3] B. Pato-Doldán, L. C. Gómez-Aguirre, J. M. Bermúdez-García, et al. *RSC Adv.*, 2013, **3**, 22404.

[4] J. Y. Lee, S. Ling, S. P. Argent, et al. *Chem Sci.*, 2021, **12**, 3516.

Efficient electronic passivation schemes for surface calculations of semiconductors exhibiting spontaneous polarization

Su-Hyun Yoo[1], Mira Todorova[2], Liverios Lymperakis[3], Chris Van de Walle[4] and Jörg Neugebauer[2]

[1] Department of Materials, Imperial College London, United Kingdom,

[2] Department of Computational Materials Design, Max-Planck-Insitut für Eisenforschung GmbH, Düsseldorf, Germany,

[3] Department of Physics, University of Crete, Crete, Greece

[4] Computational Materials Group, Materials Department, UCSB, USA.

Semiconductor surfaces play a central role in modern technology related to catalysis, electronics, and energy applications. The most widespread approach to study surfaces with density-functional theory calculations is to use slab geometries with periodic boundary conditions. A common strategy employed to avoid artificial charge transfer from one side of the slab to another, is to passivate the dangling bonds at its backside. Using the examples of wurtzite polar and semipolar surfaces, we demonstrate that the conventional passivation scheme using pseudo-H atoms fails to describe the electronic structure of low-symmetry semiconductors. We, therefore, developed an improved passivation method [npj Comp. Mater. 7, 58 (2021)/PR Mater. 5, 044605 (2021)] that takes the polarization effect and the concept of surface reconstructions into account. It accurately describes surface electronic properties and enables computationally efficient surface energy calculations. Using this novel approach we have studied the orientation-dependent thermodynamic stability and electronic properties of GaN surfaces. The resulting Wulff shape provides insight into how to avoid facet-related defects such as V-pits hampering GaN-based electronics.

Defect rocksalt structures in the La-Na-N system

Yao Yuan,[1] Simon D. Kloß[2] and J. Paul Attfield.[1]

[1] Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Edinburgh, UK,

[2] Department of Chemistry, Ludwig-Maximilians-Universität München, Munich, Germany.

Nitride materials have important applications in ceramics, optoelectronics, and phosphors. However synthesis of solid nitrides, and in particular those with high nitrogen contents, is challenging because of the stability and inertness of the N_2 molecule. Sodium azide (NaN_3) is a versatile nitrogen source and it has recently been shown that high pressure high temperature (HPHT) reactions using NaN_3 can lead to the synthesis of stoichiometric ternary nitrides of transition metals in high oxidation states such as Ca_4FeN_4, Ca_2NiN_2, and $LaReN_3$.[1-3] Decomposition of NaN_3 results both in a high nitrogen activity and metallic Na to act as a flux, but there is the possibility that Na could be incorporated into a product phase. Although no Na was found within the latter materials, we have investigated this possibility through HPHT reactions of NaN_3 with a simple nitride, LaN, to discover whether ternary Na-containing products can be formed.

Reactions between lanthanum nitride (LaN) and sodium azide (NaN_3) at 800 °C under 8 GPa pressure have led to the discovery of two defect rocksalt phases which are the first reported ternaries in the La-Na-N system. One phase is $La_{1-x}Na_{3x}N$ with vacancies at octahedral La sites and interstitial tetrahedral Na cations. This phase has a tetragonally distorted rocksalt structure (space group $I4/mmm$, a = 3.8704(2) and c = 5.2098(3) Å for $x = 0.10$) and the distortion decreases with increasing Na content, giving a cubic $Fm\bar{3}m$ phase (a = 5.3055(2) Å) for nominal $x = 0.25$. The latter composition coexists with another cubic $Fm\bar{3}m$ phase (a = 5.1561 (5) Å) that is based on a rocksalt type form of Na_3N with N-vacancies, '$NaN_{1/3}$', stabilised by a small amount of La at interstitial sites; $NaLa_yN_{(1+3y)/3}$ with $y < 1\%$. These initial investigations reveal that the high pressure La-Na-N phase diagram may be rich in defect rocksalt type materials.

References

[1] S. D. Kloß, A. Haffner, P. Manuel, M. Goto, Y. Shimakawa and J. P. Attfield, *Nat. Commun.* 2021, **12**, 571.

[2] S. D. Kloß and J. P. Attfield, *Chem. Commun.* 2021, **57**, 10427-10430.

[3] S. D. Kloß, M. L. Weidemann and J. P. Attfield, *Angew. Chem. Int. Ed.* 2021, **60**, 22260-22264.

Characterization of the electronic and photovoltaics properties of zinc and silicon phthalocyanines with possible application to solar cells. Theoretical approach.

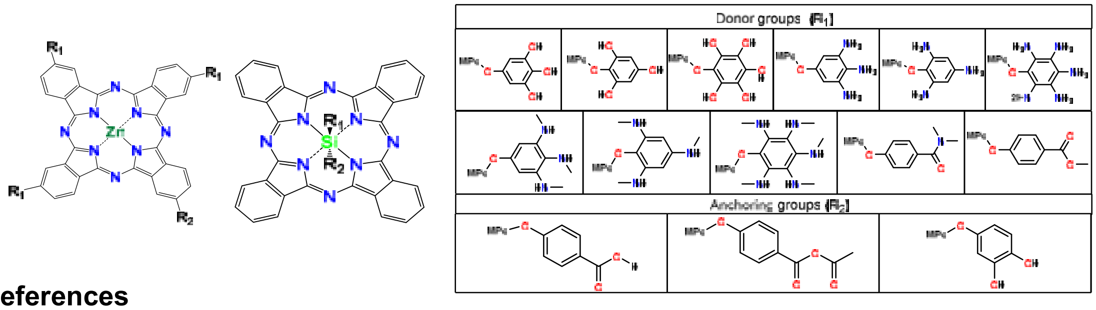
Michael Zambrano-Angulo[1], Gloria Cárdenas-Jiron[1]

[1] 1Laboratory of Theoretical Chemistry, Faculty of Chemistry and Biology, University of Santiago de Chile (USACH), Santiago, Chile.

There is currently a great demand for energy worldwide, driven by the growth of the world's population. Therefore, it is necessary to search for new energy sources. One of them is dye-sensitized solar cells, where organic precursors like phthalocyanines play an important role. Phthalocyanines (Pcs) with divalent metals such as Zinc have been widely used, however, Pcs with tetravalent metals have been less studied. Hence, Zn and Si Pcs with periplanar and axial substituents, respectively, **(Figure 1)** have been designed.

Donor groups (hydroxyl, primary amines, secondary amines, amide, and ester) and different anchoring groups (carboxyl, anhydrous and catechol), shown in **Figure 1** were evaluated. These modifications are produced to be evaluated for possible application in dye-sensitized solar cells. The effect of these modifications on the electronic, optical, and photovoltaic properties in each of the 66 molecules has been investigated from a theoretical point of view. Fully optimized molecular structures at the B3LYP/6-31G(d,p) level of theory with Grimme's dispersion show non-planar systems suggesting a lower tendency to aggregation of phthalocyanines. According to the Natural bond orbital (NBO) analysis, it was found an intramolecular charge transfer from carbons to indole nitrogen and azo bridges, in addition, it was evidenced that the indole nitrogen has less charge to directly bonded to the metal. Electrostatic potential maps show a concentration of electrons in the substituent groups, thus showing the donor effect on the system. In addition, the optical properties showed the characteristic bands, an intense band Q close to 700 nm and the B band around 350 nm. Compound 9 with silicon and the anhydrous anchoring group is the one that presents a greater wavelength. In the photovoltaics properties, it was also found that all structures have ground state oxidation potential (GSOP) and excited state oxidation potential (ESOP) values bigger than the redox potential of the electrolyte and conduction band of the semiconductor (TiO_2), respectively, suggesting a better injection of electrons between dye and semiconductor. Considering the electron injection, ZnPc exhibit higher values compared to SiPc, with primary amine and secondary amine substituents.

Figure 1. Molecular structure of the systems studied.



References

- Urbani, M., et al., Phthalocyanines for dye-sensitized solar cells. Coord. Chem. Rev., (2019) **381**, 1-64
- Vebber, M., et al., Bis (trialkylsilyl oxide) silicon phthalocyanines: Understanding the role of solubility in device performance as ternary additives in organic photovoltaics. Langmuir, (2020). **36**(10), 2612-2621

Orbital Orientation-based Theoretical Design of Single-Atom Catalysts for the Hydrogen Evolution Reaction

Fengchu Zhang,[1] Ding Yi,[2] Xi Wang[3] and Sha Li*.[4]

[1] Department of Physics, School of Science,
Beijing Jiaotong University, Beijing 100044, P. R. China,
[2] Department of Physics, School of Science,
Beijing Jiaotong University, Beijing 100044, P. R. China,
[3] Department of Physics, School of Science,
Beijing Jiaotong University, Beijing 100044, P. R. China,
[4] Chemistry and Chemical Engineering Guangdong
Laboratory, Shantou 515031, P. R. China.

As a clean fuel with high calorific value, hydrogen produced from sustainable technologies is thought to alleviate energy crisis and global warming issues. Hydrogen evolution reaction (HER) is one of the most effective means to produce hydrogen. But it usually suffers from the lack of the novel design concept of high-efficiency catalysts, especially, in neutral condition. Herein we proposed an orbital-orientation-based theoretical design concept for the efficient single-atom HER catalysts. Through screening 14 catalysts consisting of the transition metal single-atom doped into TiO_2 ($TM_1@TiO_2$) nanosheets, we demonstrate that the d orbital orientation of TM_1-Ti_1 atomic pairs plays a key role in the regulation of catalytic activities. Among them, $Pd_1@TiO_2$ is screened out as an excellent HER catalyst in neutral media, where the Pd-$d_{x^2-y^2}$ orbital tends to be exposed due to existence of Pd_1-Ti_1 atomic pair and thus promotes OH desorption and the overall hydrogen production. This work provides a new insight through tailoring high-performance orbital catalysts and sheds an orbital-level understanding of HER mechanism.

References

[1] Z. Fengchu, X. Weiwei, Z. Na, L. Sha and W. Xi, *Appl. Surf. Sci.*, 2022, **598**, 153873.

[2] Y. Ding, L. Fei, Z. Fengchu, L. Shoujie, Z. Bo, G. Denglei, W. Xi, Y. Jiannian, *Angew. Chem. Int. Ed.*, 2020, **59**, 15855-15859.

Magnetoelectric coupling of rare-earth orthotantalates

X. Zhang[1], N.D. Kelly[2], C. Liu[1], S.E Dutton[1], S.S. Saxena[1]

[1] Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom

[2] Department of Chemistry, University of Oxford, Oxford, United Kingdom

Quantum multiferroic materials form a new and emerging area of physics where one expects to find emergence of novel quantum phases induced by subtle coupling between spin and charge degrees of freedom at low temperatures [1-2]. Experimental study of such phenomena is limited by the lack of model materials where magnetism and dielectric properties can be tuned using magnetic fields at low temperatures.

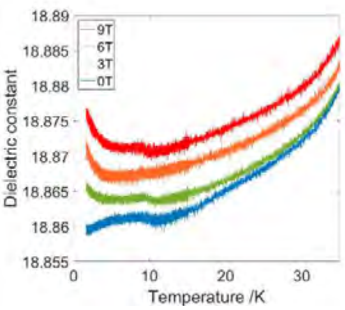


Fig. 1a: Increase of ε_r with applied field below the magnetic transition temperature of 2.25 K.

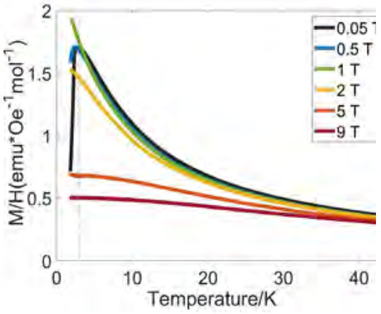


Fig. 1b: Susceptibility curves in applied field. Transformation from AFM to FM with increasing field.

In a recent breakthrough, we found that $TbTaO_4$ exhibits enhancement in dielectric response below 2 K on application of magnetic field, indicating magnetoelectric coupling. Previously, using susceptibility and heat capacity measurements we showed that $TbTaO_4$ orders at T_N = 2.25 K; powder neutron diffraction (PND) was used to solve the magnetic structure, which is A-type antiferromagnetic [3].

These measurements were conducted on polycrystalline M-$TbTaO_4$. These samples were synthesised by a solid-state reaction method at 1500 ºC. The zero-field magnetic heat capacity showed a sharp λ-type transition, typical of three-dimensional antiferromagnetic long-range ordering, at T_N = 2.25 K, [3]. Variable-temperature and variable-field PND experiments were carried out at the Institut Laue-Langevin and Paul Scherrer Institute respectively. Rietveld refinement revealed a commensurate k = 0 magnetic structure with Tb^{3+} spins parallel to the a-axis at 1.5K, Fig. 2. The onset of ordering is consistent with the heat capacity data and almost the full Tb moment of 9 μB/formula unit is recovered by 1.5 K [3]. With increasing magnetic field, the Antiferromagnetically ordered Tb^{3+} spins are initially canted away from the a-axis and then gradually align towards the a-axis, resulting in onset of Ferromagnetic order.

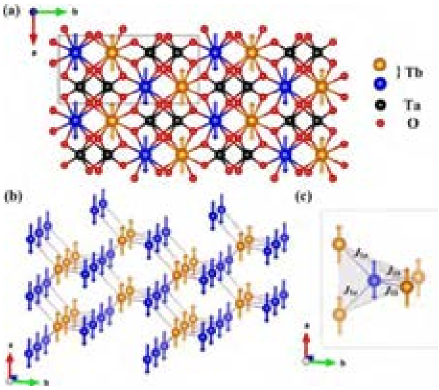


Fig. 2: Magnetic structure of $TbTaO_4$ showing the antiferromagnetic nearest-neighbour interactions [3].

References
[1] C. Morice et al., Physical Review B 96(24), 245104 (2017).
[2] A. Narayan et al., Nature Materials 18(3), 223-228 (2019).
[3] N. D. Kelly et al., Physical Review Materials 6, 044410 (2022).

Synthesis of mixed-metal cerium/zirconium UiO-66 and derived materials

Baiwen Zhao,[1] **Richard I. Walton**[1]

[1] Department of Chemistry, University of Warwick, Coventry, UK

*Corresponding author: r.i.walton@warwick.ac.uk

In the family of MOFs, the zirconium material UiO-66 is known for its exceptional stability.[1] The introduction of cerium into UiO-66 may give different properties, such as the redox activity of Ce^{4+} that can be used for catalysis.[2]

In this work, mixed-metal cerium-zirconium UiO-66 samples with different Ce/Zr ratios were synthesised by rapid reaction using DMF/ H_2O as solvents. The Ce/Zr ratios were controlled by the amount of precursors used. The materials were studied by powder X-ray diffraction (PXRD), thermogravimetric analyses (TGA) and inductively coupled plasma optical emission spectrometry (ICP-OES) to study their structures and actual Ce/Zr ratio.

Synthesis of mixed-metal cerium-zirconium UiO-66 was also studied by the control of reaction time and the use of different modulators. By comparing the expected and the real Ce/Zr ratio of the MOF, it is found that the Ce content is always lower than expected. This corresponds to the preferred formation of the $(CeZr_5)(OH)_6O_4$ (17 % Ce) cluster, which is apparently seen from a wide intended range of Ce/Zr ratio used in synthesis. In this work, a study using synchrotron XAFS is reported to provide quantification of the average Ce oxidation state (Ce L_{III} edge) and the Ce and Zr neighbours and bond distances (Ce, Zr K-edge). By studying the Ce and Zr K-edge on the MOF and the synthesis solution, it is found that the formation of Ce^{3+} in solution limits the uptake of Ce into the UiO-66 structure.

The Ce/Zr-UiO-66 materials were then used as precursors to prepare CeO_2-ZrO_2 solid solutions by controlled thermal decomposition which resulted in the capability of maintaining higher surface area from the porosity of MOF precursors. By providing size control and well dispersion for the confined nanoparticles, UiO-66(Ce, Zr) was also used to encapsulate metal nanoparticles.[3] Au nanoparticles immobilised within UiO-66 (Ce) synthesised by a double solvent method are studied and compared.

References

1 J. Winarta, B. Shan, S. M. McIntyre, L. Ye, C. Wang, J. Liu and B. Mu, *Cryst. Growth. Des.* 2020, **20**, 1347-1362

2 S. Smolders, K.Lomachenko, B. Bueken, A. Struyf, A. Bugaev, C. Atzori, N. Stock, C. Lamberti, M. Roeffaers, D. De Vos, *Chemphyschem*. 2018, **19**, 373-378

3 S. Abednatanzi, P. G. Derakhshandeh, H. Depauw, F. X. Coudert, H. Vrielinck, P. Van Der Voort and K. Leus, *Chemical Society Reviews*, 2019, **48**, 2535-2565.

Thermodynamics up to the melting point in a TaVCrW high entropy alloy: Systematic ab initio study aided by machine learning potentials

Ying Zhou,[1] Prashanth Srinivasan,[2] Blazej Grabowski,[2] Roger Smith,[1] Pooja Goddard[1] and Andrew Ian Duff.[3]

[1] School of Science, Loughborough University, UK,

[2] Institute of Materials Science, University of Stuttgart, Germany,

[3] Scientific Computing Department, STFC Daresbury Laboratory, UK.

Multi-principal-component alloys have attracted great interest as a novel paradigm in alloy design, with often unique properties and a vast compositional space auspicious for materials discovery. High entropy alloys (HEAs) belong to this class and are being investigated for prospective nuclear applications with reported superior mechanical properties including high temperature strength and stability compared to conventional alloys.

Here we calculate high temperature properties of the multicomponent body-centred low-activation HEA TaVCrW with DFT accuracy using a modified version of the two-stage up-sampled thermodynamic integration using Langevin dynamics (TU-TILD) approach. The proposed approach is based on density-functional theory (DFT) and thermodynamic integration combined with machine-learning based interatomic models, and in the present work improves the computational efficiency of the standard TU-TILD method by a factor of 4. The described methodology is also relevant to potential applications of HEAs in nuclear energy, and our modified formalism is well positioned for thermodynamic property prediction and high-throughput screening of multi-principal component alloys more generally. The machine learning potentials that were fitted using ab initio MD are now being tested for their applicability in radiation damage studies of HEAs. The outcome of this research will be reported at the meeting.